Thermal Expansion Property of Synthetic Cubic Leucite-Type Compounds

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Various cubic Cs-leucite compounds with the space group Ia3d were synthesized by a solid-state reaction method, and thermal expansion properties for the synthetic powders were studied in the temperature range from 123 to 1273 K using high-temperature X-ray diffraction (HTXRD) and low-temperature X-ray diffraction (LTXRD). The thermal expansion rates of both the synthetic cubic CsBa2Al3Si6O18 and cubic Cs3MgSi5O12 (M=Cd, Mg, Ni, Zn) were lower than that of the synthetic cubic CsAlSi2O6 (M=Al, Fe), and the thermal expansion rate of the synthetic cubic Cs0.8Al0.2Si2O6 was lower than that of CsAlSi2O6. Consequently, decreasing the average ionic radius of cations in the M site, or increasing the Si/M molar ratio of the (Si, M)O4 tetrahedra was found to be effective for decreasing the thermal expansion rate. Furthermore, it was suggested that the increase of the space for Cs sites in the unit cell decreases the thermal expansion rate of the cubic Cs-leucite compounds with the space group Ia3d.

Key-words: Leucite, Thermal expansion property, Phase transition, Ionic radius

1. Introduction

The Cs-leucite compound with the space group Ia3d, CsMSi5O12 (M=Cd, Al, Fe), which is one of the cubic silicate compounds, is a low thermal expansion material in the temperature range 298 to around 873 K. The CsMSi5O12 (M=Al, Fe) unit cell has a three-dimensional framework structure which consists of 48 (Si, M)O4 tetrahedra with 16 Cs+ ions occupying large 12-coordinate cavities.

Pollucite, CsAlSi2O6, is known to be a ceramic which exhibits a unique thermal expansion behavior. The thermal expansion curve of CsAlSi2O6 has two stages; the mean linear thermal expansion coefficient of the first stage is about 12.5 x 10^-6/K in the temperature range from 298 to 473 K, and that of the second stage is about 2.2 x 10^-6/K at 473–1473 K.7 The thermal expansion behavior of CsAl2O4 has been studied from the viewpoint of crystal structure. That is to say, some results have suggested that the behavior is due to the change of the three-dimensional aluminosilicate framework structure from "a collapsed form" to "an expanded form" by the rotation of (Si, Al)O4 tetrahedra due to increasing temperature. Cubic Cs2MSi5O12 (M=Cd, Mg, Ni, Zn) has been identified with XRD patterns, and they were heated at 973–1073 K for 20–40 h in air until the cubic Cs2MSi5O12 was completed in an Al2O3 boat.5 The synthetic cubic CsMSi2O6 (M=B, Al, Fe), have been proposed.

2. Experimental procedure

2.1 Powder synthesis of leucite-type compounds

Single phases of cubic Cs-leucite, tetragonal Rb-leucite, cubic Cs1-xRbxAl1-xSi2+xO6 (X=0, 0.1), tetragonal Rb1-xAl1-xSi2+xO6 (X=0, 0.1, 0.2) and cubic Cs7/8Rb1/8AlSi2O6 were synthesized by the solid-state reaction of the powder mixtures of γ-Al2O3, SiO2 (amorphous), CsO and/or RbNO3, which had molar ratios of Cs/Si=1.0/2.0–0.9/2.1, Rb/Si=1.0/2.0–0.8/2.2 and/or Cs(Rb)/Si=0.875(0.125)/2.0 for Cs7/8Rb1/8AlSi2O6. The powders were ball-milled for periods of 24 h in the presence of ethanol. Then, the resultant powder mixtures were dried by removing the solvent, and calcined in an Al2O3 crucible using a Tamman furnace at 873–1273 K for 24–50 h in air, followed by heating using a MoSi2 furnace at 1573–1673 K for 10–15 h in order to complete the reaction in an Al2O3 boat.5 The synthetic leucite-type compounds were identified with XRD (MX-P18VA, Mac Science, Cu Kα, 40 kV, 200 mA).

Cubic CsM1/2Al1/2Si2O6 (M=Al, Fe, B0.2Al0.8, Al0.5Fe0.5, Al0.2Fe0.8) was synthesized by the two-stage heat treatment of the powder mixtures of CsNO3, SiO2 (amorphous) and one or two of H2BO3, γ-Al2O3, and Fe2O3, where molar ratios were Cs/M=1.0/1.0, M/Si=1.0/2.0. The powder mixtures were calcined in an Al2O3 crucible at 873–973 K for 24 h in air. Then, the calcined powders were heated at 1173–1673 K for 2–10 h in air.

Cubic Cs2MSi5O12 (M=Cd, Mg, Ni, Zn) was synthesized by the two-stage heat treatment of the powder mixture of CsNO3, SiO2 (amorphous) and MO (M=Cd, Mg, Ni, Zn) derived from decomposition of the oxalate or the formate, which had molar ratios of Cs/M=2.0/1.0 and M/Si=1.0/5.0. The powder mixtures were calcined at 973–1073 K for 20–40 h in air until the cubic Cs2MSi5O12 (M=Cd, Mg, Ni, Zn) phase with the space group Ia3d was identified with XRD patterns, and then they were heated at...
Only tetragonal $\text{Rb}_1-x\text{Al}_x\text{Si}_2+X\text{O}_6$ ($X=0.1, 0.2$) required two types of calcination in the first step of the multistep heating process in order to synthesize the single phase. All of the heating conditions of the multistep heating process for the leucite-type compounds are listed in Table 1.

### 2.2 Thermal expansion properties of the synthetic leucite-type compounds

Thermal expansion properties of the synthetic leucite-type compounds were investigated from the viewpoint of the change of the lattice constant with temperature. The lattice constants of the synthetic leucite-type compounds in the temperature ranges from 123 to 298 K and 298 to 1273 K were examined using low-temperature and high-temperature X-ray diffraction equipment (Mac Science, MXP18VA, LTXRD and HTXRD, equipped with monochromator, Cu Kα), respectively. In the case of HTXRD, a measuring sample was set in a Pt holder in contact with the thermocouple, and in the case of LTXRD, one was set in an Al-alloy holder in contact with the thermocouple.

After holding the sample for 5 min, the lattice constants of the synthetic cubic leucite-type compounds of each temperature were calculated by the least-squares method with the six peaks of (332), (440), (611), (721) and (851) planes, and those of the synthetic tetragonal leucite-type compounds were calculated with the seven peaks of (314), (420), (323), (404), (532), (327) and (732) planes, which were corrected using Si as the external standard at a scanning speed of 1°/min. The thermal changes of the lattice constants were investigated in the range from 123 to 1273 K.

### 2.3 Chemical compositions of the synthetic leucite-type compounds

Chemical compositions of the synthetic leucite-type compounds were examined by fluorescent X-ray diffraction (PW2400, Philips, Japan) and ICP emitting analysis. The chemical compositions of the compounds are listed in Table 2. Numbers in parentheses are measurement errors in units of the last decimal place. Silicon and oxygen contents of the chemical formulae for the compounds were fixed at 22.2 and 6, respectively.

### Table 1. Heating Process for Leucite-Type Compounds with the Space Group $Ia\overline{3}d$

<table>
<thead>
<tr>
<th>Synthesized leucite-type compounds</th>
<th>heating process</th>
<th>heat treatment (holding time)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Cs}_2\text{Si}_2\text{O}_6$</td>
<td>$M=\text{Fe}$</td>
<td>973K (24h)</td>
</tr>
<tr>
<td>$M=\text{Al}$</td>
<td></td>
<td>1573K (10h)</td>
</tr>
<tr>
<td>$M=\text{B}_0.2\text{Al}_0.8$</td>
<td></td>
<td>923K (24h)</td>
</tr>
<tr>
<td>$M=\text{Al}_0.5\text{Fe}_0.5$</td>
<td></td>
<td>1673K (10h)</td>
</tr>
<tr>
<td>$M=\text{Al}_0.2\text{Fe}_0.8$</td>
<td></td>
<td>873K (24h)</td>
</tr>
<tr>
<td>$M=\text{B}$</td>
<td></td>
<td>1473K (10h)</td>
</tr>
<tr>
<td>$M=\text{B}_0.2\text{Al}_0.8$</td>
<td></td>
<td>923K (24h)</td>
</tr>
<tr>
<td>$M=\text{Al}_0.2\text{Fe}_0.8$</td>
<td></td>
<td>1173K (2h)</td>
</tr>
<tr>
<td>$M=\text{B}_0.2\text{Al}_0.8$</td>
<td></td>
<td>923K (24h)</td>
</tr>
<tr>
<td>$M=\text{Al}_0.2\text{Fe}_0.8$</td>
<td></td>
<td>1173K (2h)</td>
</tr>
</tbody>
</table>

### Table 2. Chemical Composition of the Synthetic Leucite-Type Compounds

<table>
<thead>
<tr>
<th>Sample</th>
<th>Chemical composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Cs}_2\text{Si}_2\text{O}_6$</td>
<td>$\text{Cs}_6\cdot\text{B}_6\cdot\text{Si}_2\cdot\text{O}_6$</td>
</tr>
<tr>
<td>$\text{Cs}_2\text{Al}_2\text{Si}_2\text{O}_6$</td>
<td>$\text{Cs}_6\cdot\text{B}_6\cdot\text{Al}_2\cdot\text{Si}_2\cdot\text{O}_6$</td>
</tr>
<tr>
<td>$\text{Cs}_{2}\text{FeSi}_2\text{O}_6$</td>
<td>$\text{Cs}_6\cdot\text{FeSi}_2\cdot\text{O}_6$</td>
</tr>
<tr>
<td>$\text{Cs}_2\text{Si}_2\text{O}_6$</td>
<td>$\text{Cs}_6\cdot\text{Si}_2\cdot\text{O}_6$</td>
</tr>
<tr>
<td>$\text{Cs}_{2}\text{Al}_2\text{Si}_2\text{O}_6$</td>
<td>$\text{Cs}_6\cdot\text{Al}_2\cdot\text{Si}_2\cdot\text{O}_6$</td>
</tr>
<tr>
<td>$\text{Cs}_{2}\text{Al}_2\text{FeSi}_2\text{O}_6$</td>
<td>$\text{Cs}_6\cdot\text{Al}_2\cdot\text{FeSi}_2\cdot\text{O}_6$</td>
</tr>
<tr>
<td>$\text{Cs}_{2}\text{Si}_2\text{O}_6$</td>
<td>$\text{Cs}_6\cdot\text{Si}_2\cdot\text{O}_6$</td>
</tr>
<tr>
<td>$\text{Cs}_2\text{MgSi}_2\text{O}_6$</td>
<td>$\text{Cs}_6\cdot\text{Mg}_2\cdot\text{Si}_2\cdot\text{O}_6$</td>
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<tr>
<td>$\text{Cs}_2\text{ZnSi}_2\text{O}_6$</td>
<td>$\text{Cs}_6\cdot\text{Zn}_2\cdot\text{Si}_2\cdot\text{O}_6$</td>
</tr>
<tr>
<td>$\text{Cs}_2\text{NiSi}_2\text{O}_6$</td>
<td>$\text{Cs}_6\cdot\text{Ni}_2\cdot\text{Si}_2\cdot\text{O}_6$</td>
</tr>
<tr>
<td>$\text{Cs}_2\text{Al}_2\text{Si}_2\text{O}_6$</td>
<td>$\text{Cs}_6\cdot\text{Al}_2\cdot\text{Si}_2\cdot\text{O}_6$</td>
</tr>
<tr>
<td>$\text{Cs}_2\text{Al}_2\text{FeSi}_2\text{O}_6$</td>
<td>$\text{Cs}_6\cdot\text{Al}_2\cdot\text{FeSi}_2\cdot\text{O}_6$</td>
</tr>
<tr>
<td>$\text{Rb}_2\text{Al}_2\text{Si}_2\text{O}_6$</td>
<td>$\text{Rb}_6\cdot\text{Al}_2\cdot\text{Si}_2\cdot\text{O}_6$</td>
</tr>
<tr>
<td>$\text{Rb}_2\text{Al}_2\text{FeSi}_2\text{O}_6$</td>
<td>$\text{Rb}_6\cdot\text{Al}_2\cdot\text{FeSi}_2\cdot\text{O}_6$</td>
</tr>
</tbody>
</table>

3. Results and discussion

3.1 Thermal expansion property of cubic $\text{CsMSi}_2\text{O}_6$ with molar ratio of $\text{Si}/M=2$ ($M=\text{B}, \text{B}_0.2\text{Al}_0.8, \text{Al}, \text{Al}_0.5\text{Fe}_0.5, \text{Al}_0.2\text{Fe}_0.8, \text{Fe}$)

There was a small difference between the intensities of each diffraction line in the XRD pattern at 298 K for synthetic $\text{CsMSi}_2\text{O}_6$ ($M=\text{B}, \text{B}_0.2\text{Al}_0.8, \text{Al}, \text{Al}_0.5\text{Fe}_0.5, \text{Al}_0.2\text{Fe}_0.8, \text{Fe}$). Synthetic $\text{CsMSi}_2\text{O}_6$ ($M=\text{B}, \text{B}_0.2\text{Al}_0.8, \text{Al}, \text{Al}_0.5\text{Fe}_0.5, \text{Al}_0.2\text{Fe}_0.8, \text{Fe}$) was identified to be cubic with the space group $Ia\overline{3}d$, upon comparison with the XRD pattern of cubic $\text{CsAl}_2\text{Si}_2\text{O}_6$ ($M=\text{B}, \text{Al}, \text{Fe}$). Cubic Cs-leucite compounds with molar ratios of more than $\text{Al}/M=4$ or more than $\text{Al}/\text{Fe}=1$ could not be synthesized. These experimental results suggest that it is very difficult to form the $(\text{Si}, \text{M})\text{O}_4$ framework structure of cubic Cs-leucite compounds by the solid-state reaction.

Figure 1 shows the thermal expansion property of cubic $\text{CsMSi}_2\text{O}_6$ ($M=\text{B}_0.2\text{Al}_0.8, \text{Al}_0.5\text{Fe}_0.5, \text{Al}_0.2\text{Fe}_0.8, \text{Fe}$) at 298–1073 K compared with that of cubic $\text{CsSi}_2\text{O}_6$ ($M=\text{B}, \text{Al}, \text{Fe}$) represented by the dashed line. The thermal expansion property of the cubic $\text{CsMSi}_2\text{O}_6$ ($M=\text{B}, \text{Al}, \text{Fe}$) was identical to that in a previous report. Cubic $\text{CsAl}_{0.5}\text{Fe}_{0.5}\text{Si}_2\text{O}_6$, having $\text{Al}_0.2\text{Fe}_0.8$ substituted for Fe in the $M$ site of $(\text{Si}, \text{M})\text{O}_4$.
tetrahedra of cubic CsFeSi$_2$O$_6$ had a lower thermal expansion rate than that of cubic CsFeSi$_2$O$_6$. The thermal expansion rate of cubic CsAl$_{0.9}$Si$_2$O$_6$, with Al$_{0.9}$Si$_{2.1}$O$_6$ substituted for Al in the M site of (Si, M)O$_4$ tetrahedra of cubic CsAlSi$_2$O$_6$, had a lower thermal expansion rate than cubic CsAlSi$_2$O$_6$, and the thermal expansion rate of cubic CsMSi$_5$O$_{12}$ (M = B$_2$Al$_{0.8}$) was similar to that of cubic CsBSi$_5$O$_{12}$.

On the basis of the above-mentioned results, it was found that the substitution of B for Al in the Al site for the (Si, Al)$_2$O$_4$ tetrahedra of cubic CsAlSi$_2$O$_6$ or Al for Fe of the Fe site for the (Si, Fe)$_2$O$_4$ tetrahedra of cubic CsFeSi$_2$O$_6$ was effective in decreasing the thermal expansion rate of the cubic Cs-leucite compound. This result confirmed that the thermal expansion property depended on the change of the (Si, M)O$_4$ framework structure upon replacing M in the unit cell of the cubic Cs-leucite compound, and that it was possible to control the thermal expansion property of cubic Cs-leucite compounds by changing the chemical composition of the (Si, M)O$_4$ tetrahedra of the framework structure.

3.2 Thermal expansion property of cubic Cs$_2$MSi$_5$O$_{12}$ with molar ratio of Si/M = 5 (M = Cd, Mg, Ni, Zn)

Although there was a difference between the intensities of the diffraction lines in the XRD pattern for synthetic Cs$_2$MSi$_5$O$_{12}$ (M = Cd, Mg, Ni, Zn) and cubic CsMSi$_5$O$_{12}$ (M = B, Al, Fe), synthetic Cs$_2$MSi$_5$O$_{12}$ (M = Cd, Mg, Ni, Zn) was clearly cubic with the space group Ia$3d$, based on the diffraction lines of its XRD patterns in comparison with those of cubic CsMSi$_5$O$_{12}$ (M = B, Al, Fe) with the space group Ia$3d$. Figure 2 shows the thermal expansion property of cubic Cs$_2$MSi$_5$O$_{12}$ (M = Cd, Mg, Ni, Zn) in the range from 298-1273 K. It exhibited an almost linear relationship between the thermal expansion rate and temperature, and the thermal expansion rates were lower than those of cubic CsMSi$_5$O$_{12}$ (M = Al, Fe). The thermal expansion properties were differed, but the difference between the properties was not so great as in the case of the cubic CsMSi$_5$O$_{12}$. The result suggests that the influence of the change of M on the thermal expansion property decreased with increasing Si/M molar ratio of the (Si, M)O$_4$ tetrahedra of the framework structure. Moreover, because the thermal expansion rate of cubic CsNiSi$_5$O$_{12}$ in the range from 773-973 K is similar to that of cubic CsAlSi$_5$O$_{12}$ in the range from 473-773 K, the lower thermal expansion property of cubic CsAlSi$_5$O$_{12}$ is not a unique property. Cubic Cs$_2$MSi$_5$O$_{12}$ (M = B, Al, Fe) at 298 K has the lattice constants of $a = 1.2991$ nm for M = B, $a = 1.3680$ nm for M = Al, $a = 1.3840$ nm for M = Fe. On the other hand, cubic Cs$_2$MSi$_5$O$_{12}$ (M = Cd, Mg, Ni, Zn) at 298 K has the lattice constants of $a = 1.3780$ nm for M = Cd, $a = 1.3679$ nm for M = Mg, $a = 1.3640$ nm for M = Ni and $a = 1.3658$ nm for M = Zn. The relationship between the lattice constant and the ionic radius of M of the (Si, O)O$_4$ tetrahedra for the synthetic cubic Cs-leucite compound with the space group Ia$3d$ is shown in Fig. 3. The lattice constant at 298 K increased with increasing ionic radius of the M cation. The thermal expansion rate of the cubic Cs-leucite compounds increased with increasing temperature. Considering that the Si/M molar ratio of the (Si, M)O$_4$ tetrahedra of Cs$_2$MSi$_5$O$_{12}$ (M = Al, Fe) was 2 and that of Cs$_2$MSi$_5$O$_{12}$ (M = Cd, Mg, Ni, Zn) was 5, it was found that the increase of the Si/M molar ratio of (Si, M)O$_4$ tetrahedra was effective in decreasing the thermal expansion rate of the cubic Cs-leucite compounds.

3.3 Thermal expansion property of cubic Cs$_{0.9}$Al$_{0.9}$Si$_2$O$_6$ with vacant Cs site

The crystalline system of synthetic Cs$_{0.9}$Al$_{0.9}$Si$_2$O$_6$ was considered to be cubic with the space group Ia$3d$ at 298 K, based on the XRD patterns. The change of the XRD patterns in the range from 298-1273 K was investigated by HTXRD. Since the diffraction angle $2\theta$ in the XRD pattern of synthetic cubic Cs$_{0.9}$Al$_{0.9}$Si$_2$O$_6$ only decreased with increasing temperature due to thermal expansion without a structural phase transition, synthetic Cs$_{0.9}$Al$_{0.9}$Si$_2$O$_6$ was considered to be cubic with the space group Ia$3d$ above 298 K. The thermal expansion property of cubic Cs$_{0.9}$Al$_{0.9}$Si$_2$O$_6$ in the range from 298-1273 K was investigated by HTXRD and the results are shown with those of cubic CsAlSi$_2$O$_6$ in Fig. 4. Cubic CsAlSi$_2$O$_6$ and Cs$_{0.9}$Al$_{0.9}$Si$_2$O$_6$ had the lattice constants of $a = 1.3681$ nm and $a = 1.3679$ nm at 298 K, respectively. As shown in Fig. 4, the thermal expansion rate of cubic Cs$_{0.9}$Al$_{0.9}$Si$_2$O$_6$ in the range from 298-1273 K was lower than that of cubic CsAlSi$_2$O$_6$. It was considered that the lower thermal expansion property of cubic Cs$_{0.9}$Al$_{0.9}$Si$_2$O$_6$ above 298 K was due to the shift of the temperature range of the larger thermal expansion proper-
ty to a lower temperature range. On the other hand, the
temperature range of that of cubic CsAlSi2O6 was from 298
to 473 K.

The XRD patterns of CsAlSi2O6 and Cs0.9Al0.9Si2.1O6 in
the range from 123–298 K were investigated by LTXRD.
The results are shown in Figs. 5 and 6. The diffraction
lines of CsAlSi2O6 were split below 248 K, while the diffrac-
tion lines of Cs0.9Al0.9Si2.1O6 were split below 173 K, which
is about 75 K lower than the temperature for CsAlSi2O6,
and exhibited changes of the diffraction lines due to the
structural phase transition from tetragonal to cubic7),10,11) with increasing temperature. Therefore, it was concluded
that CsAlSi2O6 and Cs0.9Al0.9Si2.1O6 undergo a structural
phase transition from tetragonal to cubic, and that the struc-
tural phase transition temperatures are around 248 K and
173 K, respectively.

As shown in Fig. 7, the lattice constant for tetragonal
CsAlSi2O6 of the a-axis increased and that of the c-axis
decreased with increasing temperature from 123 to 273 K.
Consequently, cubic CsAlSi2O6 showed a larger thermal
expansion at 273–473 K. Tetragonal Cs0.9Al0.9Si2.1O6 also
showed that the lattice constant of the a-axis increased
and that of the c-axis decreased with increasing temperature at
123–173 K. Cubic Cs0.9Al0.9Si2.1O6 showed the larger ther-
amal expansion in the range from 173–323 K after undergo-
ing the structural phase transition. The mean linear thermal
expansion coefficient of cubic Cs0.9Al0.9Si2.1O6 in the range
from 298–1273 K was $2.05 \times 10^{-6}/K$. In comparison with
the mean linear thermal expansion coefficient of cubic CsB
Si2O6 of $2.75 \times 10^{-6}/K$ in the range from 298–1073 K, it
was suggested that cubic Cs0.9Al0.9Si2.1O6 had a lower ther-
amal expansion rate than that of cubic CsBSi2O6 above 298
K, as shown in Fig. 4. The thermal expansion property of
cubic Cs0.9Al0.9Si2.1O6 in the range from 298–1273 K was similar
in shape to that of CsAlSi2O6 in the range from 298–1273 K.
Therefore, it was concluded that the lower thermal expan-
sion property of cubic Cs0.9Al0.9Si2.1O6 in the range from
298–1273 K was due to the structural phase transition
temperature, which is about 75 K lower than that of
CsAlSi2O6, in addition to the larger thermal expansion of
Cs0.9Al0.9Si2.1O6. On the other hand, synthetic CsMSi2O6
(M=B, Fe) did not undergo a structural phase transition,
even at a lower temperature.

The lattice constants of synthetic RbAlSi2O6, Rb0.9Al0.9
Si2.1O6, and Rb0.8Al0.8Si2.2O6 in the temperature range from
298 to 1273 K are shown in Fig. 8. The crystalline systems
of Rb0.9Al0.9Si2.1O6 and Rb0.8Al0.8Si2.2O6 were found to be
tetragonal with the space group $I4_1/a$ at 298 K upon com-
parison with the XRD pattern of tetragonal RbAlSi2O6. The
lattice constants of the a-axis increased and those of the c-
axis decreased with increasing temperature, as did those of
tetragonal RbAlSi2O6 and tetragonal Cs-leucites. The struc-
tural phase transition temperature decreased with decreas-
ing number of Rb+ ions of Rb-leucites, and also the thermal
expansion rate of cubic Rb-leucite in the range from 673–
1273 K decreased with decreasing number of Rb+ ions
of Rb-leucite. On the basis of the above-mentioned result, it
was concluded that the tendency for the decrease of the
Thermal Expansion Property of Synthetic Cubic Leucite-Type Compounds

The phase transition temperature of Cs-leucites or Rb-leucites is due to the decrease of the number of alkaline cations of Cs-leucites or Rb-leucites, and that this tendency is the same as the behavior of the cubic leucite-type compounds. Therefore, it is considered that the lattice constant of the cubic leucite-type compounds decreases with decreasing structural phase transition temperature.

The lattice constants of synthetic cubic CsAlSi\(_2\)O\(_6\), Cs\(_{0.9}\)Al\(_{0.9}\)Si\(_{2.1}\)O\(_6\), and Cs\(_{7/8}\)Rb\(_{1/8}\)AlSi\(_2\)O\(_6\) at 298–1273 K were investigated by HTXRD. The results are shown in Fig. 9. The lattice constant of a=1.3654 nm for cubic Cs\(_{0.9}\)Rb\(_{1/8}\)AlSi\(_{2}\)O\(_6\) at 298 K was smaller than that of a=1.3682 nm for cubic CsAlSi\(_2\)O\(_6\). This was because the unit cell of cubic Cs\(_{0.9}\)Rb\(_{1/8}\)AlSi\(_{2}\)O\(_6\) had Rb\(^+\) ions replaced with 12.5 mol\% of Cs\(^+\) ions in the unit cell of cubic CsAlSi\(_2\)O\(_6\). On the other hand, the lattice constant of a=1.3679 nm for cubic Cs\(_{0.9}\)Al\(_{0.9}\)Si\(_{2.1}\)O\(_6\) with Cs vacant sites replaced with 10 mol\% of Cs\(^+\) ions in the unit cell of cubic CsAlSi\(_2\)O\(_6\) was almost the same as that of cubic CsAlSi\(_2\)O\(_6\) without decreasing lattice constant at 298 K.

It has been proposed in some reports\(^3\),\(^7\) that the larger thermal expansion of cubic CsAlSi\(_2\)O\(_6\) in the range from 298–473 K is due to the structural change from “a collapsed state” to “an expanded state” of a three-dimensional aluminosilicate framework at 298 K through the change of the bond angles of (Si, Al)O\(_4\) tetrahedra in the unit cell. Since it is considered that CsAlSi\(_2\)O\(_6\) and Cs\(_{7/8}\)Rb\(_{1/8}\)AlSi\(_2\)O\(_6\) had 16 bonds between 16 alkaline cations and 16 AlO\(_4\)\(^-\) tetrahedra in the unit cell, and Cs\(_{0.9}\)Al\(_{0.9}\)Si\(_{2.1}\)O\(_6\) had 16\(\times\)0.9 (=14.4) bonds between 16\(\times\)0.9 (=14.4) alkaline cations and 16\(\times\)0.9 (=14.4) AlO\(_4\)\(^-\) tetrahedra in the unit cell, it was suggested that the number of Cs\(^+\) ions of Cs-leucite controlled the structural state of the three-dimensional aluminosilicate framework of Cs-leucite at 298 K. Consequently, the lower thermal expansion property of synthetic cubic Cs\(_{0.9}\)Al\(_{0.9}\)Si\(_{2}\)O\(_6\) in the range from 298–1273 K was due to “an expanded state” at 298 K to a greater degree than that of CsAlSi\(_2\)O\(_6\) which was influenced by a three-dimensional aluminosilicate framework with 16\(\times\)0.9 (=14.4) bonds between Cs\(^+\) ions and the AlO\(_4\)\(^-\) tetrahedra of Cs\(_{0.9}\)Al\(_{0.9}\)Si\(_{2}\)O\(_6\).

Figure 10 shows the relationship between the average ionic radius and the lattice constants of the synthetic cubic leucite-type compounds. The average ionic radius was calculated using Eq. (1) for CsMSi\(_2\)O\(_6\) (M=B, Al, Fe, B\(_{0.2}\)Al\(_{0.8}\)Fe\(_{0.2}\)) and Cs\(_{0.9}\)Al\(_{0.9}\)Si\(_{2}\)O\(_6\), or Eq. (2) for Cs\(_2\)MSi\(_5\)O\(_{12\}}\) (M=Ni, Mg, Zn, Cd).

Average ionic radius
\[\text{Average ionic radius} = \frac{\text{Average ionic radius of } \#W\text{Si}^4+ \text{ ion}}{3} \times 2 + \frac{\text{Average ionic radius of } \#W\text{M}^{3+} \text{ ion}}{3}\] (1)

Average ionic radius
\[\text{Average ionic radius} = \frac{\text{Average ionic radius of } \#W\text{Si}^4+ \text{ ion} \times 5 + \text{Average ionic radius of } \#W\text{M}^{3+} \text{ ion}}{6}\] (2)

Here, IV is the coordination number. The lattice constant was found to increase with increasing average ionic radius for the (Si, M)O\(_4\) tetrahedra. In view of the relationship between average ionic radius and the lattice constant, it is interesting that Cs\(_{0.9}\)Al\(_{0.9}\)Si\(_{2}\)O\(_6\) showed the lower thermal expansion rate mentioned above. The unit cell of Cs\(_{0.9}\)Al\(_{0.9}\)Si\(_{2}\)O\(_6\) had the larger space than that of others due to the Cs vacant site, which was not occupied by atoms. Therefore, it was considered that cubic leucite-type compounds with the space group Ia\(_{3d}\) required a space in the unit cell in order to exhibit the lower thermal expansion property.

4. Conclusion

Various cubic Cs-leucite compounds were synthesized by the solid-state reaction, and then the thermal expansion pro-
The properties of the synthetic powders in the temperature range from 123 to 1273 K were studied by HTXRD and LTXRD. It was found that certain effective factors were required in order to decrease the thermal expansion rate of the cubic Cs-leucite compounds.

The results obtained can be summarized as follows.

1. Synthetic cubic CsB0.2Al0.8Si2O6 had a lower thermal expansion rate than cubic CsAlSi2O6, and also, both synthetic cubic CsAl0.5Fe0.5Si2O6 and CsAl0.2Fe0.8Si2O6 had lower thermal expansion rates than cubic CsFeSi2O6.

2. Synthetic cubic Cs2MSi5O12 (M=Cd, Mg, Ni, Zn) with the molar ratio of Si/M=5 had a lower thermal expansion rate. This property of Cs2MSi5O12 (M=Cd, Mg, Ni, Zn) was clearly different from that of CsMSi2O6 (M=B, Al, Fe) with the molar ratio of Si/M=2, and there was a linear relationship between the thermal expansion rate and the temperature in the temperature range from 298 to 1273 K.

3. Synthetic cubic Cs0.9Al0.9Si2.1O6 showed a lower thermal expansion than synthetic cubic CsAlSi2O6, and had the mean linear thermal expansion coefficient of 2.05×10^-6/K in the temperature range from 298 to 1273 K.

4. It was found that decreasing of the average ionic radius of cations in the M site or increasing of the molar ratio of Si/M of the (Si, M)O4 tetrahedra was effective in decreasing the thermal expansion rate of the cubic Cs-leucite compound. In addition, it was suggested that the increase of the vacant space for Cs sites in the unit cell was effective in decreasing the thermal expansion rate of the cubic Cs-leucite compounds with the space group Ia3d.

References