

## Thermal Expansion Property of Synthetic Cubic Leucite-Type Compounds

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## 合成した立方晶系リュースイト型化合物の熱膨張特性

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Various cubic Cs-leucite compounds with the space group  $Ia\bar{3}d$  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  $\text{CsB}_{0.2}\text{Al}_{0.8}\text{Si}_2\text{O}_6$  and cubic  $\text{Cs}_2\text{MSi}_5\text{O}_{12}$  ( $M = \text{Cd}, \text{Mg}, \text{Ni}, \text{Zn}$ ) were lower than that of the synthetic cubic  $\text{CsMSi}_2\text{O}_6$  ( $M = \text{Al}, \text{Fe}$ ), and the thermal expansion rate of the synthetic cubic  $\text{Cs}_{0.9}\text{Al}_{0.9}\text{Si}_{2.1}\text{O}_6$  was lower than that of  $\text{CsAlSi}_2\text{O}_6$ . Consequently, decreasing the average ionic radius of cations in the M site, or increasing the Si/M molar ratio of the (Si, M)O<sub>4</sub> 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  $Ia\bar{3}d$ . [Received June 7, 1999; Accepted October 7, 1999]

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## 1. Introduction

The Cs-leucite compound with the space group  $Ia\bar{3}d$ ,  $\text{CsMSi}_2\text{O}_6$  ( $M = \text{B}, \text{Al}, \text{Fe}$ ), which is one of the cubic silicate compounds, is a low thermal expansion material in the temperature range of 298 to around 873 K. The  $\text{CsMSi}_2\text{O}_6$  ( $M = \text{B}, \text{Al}, \text{Fe}$ ) unit cell has a three-dimensional framework structure which consists of 48 (Si, M)O<sub>4</sub> tetrahedra with 16 Cs<sup>+</sup> ions occupying large 12-coordinate cavities.<sup>1)-3)</sup>

Pollucite,  $\text{CsAlSi}_2\text{O}_6$ , is known to be a ceramic which exhibits a unique thermal expansion behavior. The thermal expansion curve of  $\text{CsAlSi}_2\text{O}_6$  has two stages; the mean linear thermal expansion coefficient of the first stage is about  $12.5 \times 10^{-6}/\text{K}$  in the temperature range from 298 to 473 K, and that of the second stage is about  $2.2 \times 10^{-6}/\text{K}$  at 473–1473 K.<sup>3),4)-6)</sup> The thermal expansion behavior of  $\text{CsAlSi}_2\text{O}_6$  has been studied from the viewpoint of crystal structure. That is to say, some results<sup>3),7)</sup> 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)O<sub>4</sub> tetrahedra due to increasing temperature. Cubic  $\text{Cs}_2\text{MSi}_5\text{O}_{12}$  ( $M = \text{Cd}, \text{Mg}, \text{Ni}, \text{Zn}$ ) with the space group  $Ia\bar{3}d$  has a three-dimensional framework structure which consists of 8 MO<sub>4</sub><sup>-</sup> tetrahedra and 40 SiO<sub>4</sub> tetrahedra, and has been known to have a linear relationship between its thermal expansion rate and temperature. The crystalline system was cubic in the temperature range above 298 K.<sup>8)</sup> Therefore, it was suggested that the thermal expansion property of the cubic leucite-type compound depends on the framework structure.

In this work, the thermal expansion property of leucite-type compounds with various chemical compositions synthesized by the solid-state reaction method and the thermal change of the lattice constant have been studied using powder high-temperature and low-temperature X-ray

diffraction analyses. Moreover, chemical compositions of the cubic leucite-type compounds, which are considered to achieve the thermal expansion rate lower than that of cubic  $\text{CsMSi}_2\text{O}_6$  ( $M = \text{B}, \text{Al}, \text{Fe}$ ), have been proposed.

## 2. Experimental procedure

## 2.1 Powder synthesis of leucite-type compounds

Single phases of cubic Cs-leucite, tetragonal Rb-leucite, cubic  $\text{Cs}_{1-x}\text{Al}_{1-x}\text{Si}_{2+x}\text{O}_6$  ( $X = 0, 0.1$ ), tetragonal  $\text{Rb}_{1-x}\text{Al}_{1-x}\text{Si}_{2+x}\text{O}_6$  ( $X = 0, 0.1, 0.2$ ) and cubic  $\text{Cs}_{7/8}\text{Rb}_{1/8}\text{AlSi}_2\text{O}_6$  were synthesized by the solid-state reaction of the powder mixtures of  $\gamma\text{-Al}_2\text{O}_3$ , SiO<sub>2</sub> (amorphous), CsNO<sub>3</sub> and/or RbNO<sub>3</sub>, 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  $\text{Cs}_{7/8}\text{Rb}_{1/8}\text{AlSi}_2\text{O}_6$ . 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 Al<sub>2</sub>O<sub>3</sub> crucible using a Tamman furnace at 873–1273 K for 24–50 h in air, followed by heating using a MoSi<sub>2</sub> furnace at 1573–1673 K for 10–15 h in order to complete the reaction in an Al<sub>2</sub>O<sub>3</sub> boat.<sup>5)</sup> The synthetic leucite-type compounds were identified with XRD (MX-P18VA, Mac Science, Cu K $\alpha$ , 40 kV, 200 mA).

Cubic  $\text{CsMSi}_2\text{O}_6$  ( $M = \text{B}, \text{Al}, \text{Fe}, \text{B}_{0.2}\text{Al}_{0.8}, \text{Al}_{0.5}\text{Fe}_{0.5}, \text{Al}_{0.2}\text{Fe}_{0.8}$ ) was synthesized by the two-stage heat treatment of the powder mixtures of CsNO<sub>3</sub>, SiO<sub>2</sub> (amorphous) and one or two of H<sub>3</sub>BO<sub>3</sub>,  $\gamma\text{-Al}_2\text{O}_3$ , and Fe<sub>2</sub>O<sub>3</sub>, where molar ratios were Cs/M = 1.0/1.0, M/Si = 1.0/2.0. The powder mixtures were calcined in an Al<sub>2</sub>O<sub>3</sub> 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  $\text{Cs}_2\text{MSi}_5\text{O}_{12}$  ( $M = \text{Cd}, \text{Mg}, \text{Ni}, \text{Zn}$ ) was synthesized by the two-stage heat treatment<sup>8)</sup> of the powder mixture of CsNO<sub>3</sub>, SiO<sub>2</sub> (amorphous) and MO ( $M = \text{Cd}, \text{Mg}, \text{Ni}, \text{Zn}$ ) 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  $\text{Cs}_2\text{MSi}_5\text{O}_{12}$  ( $M = \text{Cd}, \text{Mg}, \text{Ni}, \text{Zn}$ ) phase with the space group  $Ia\bar{3}d$  was identified with XRD patterns, and then they were heated at

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1273–1573 K for 20 h in air.<sup>8)</sup>

Only tetragonal  $\text{Rb}_{1-x}\text{Al}_{1-x}\text{Si}_{2+x}\text{O}_6$  ( $X=0.1, 0.2$ ) 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  $K\alpha$ ), 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), (631), (721) and (651) 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 2–2.2 and 6, respectively.

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

Synthesized leucite-type compounds	heating process	
	calcination (holding time)	heat treatment (holding time)
$\text{CsMSi}_2\text{O}_6$		
M=Fe	973K (24h)	1573K (10h)
M= $\text{Al}_{0.2}\text{Fe}_{0.8}$	923K (24h)	1673K (10h)
M= $\text{Al}_{0.5}\text{Fe}_{0.5}$	923K (24h)	1673K (10h)
M=Al	873K (24h)	1473K (10h)
M= $\text{B}_{0.2}\text{Al}_{0.8}$	923K (24h)	1173K (2h)
M=B	923K (24h)	1173K (2h)
$\text{Cs}_2\text{MSi}_5\text{O}_{12}$		
M=Cd	973K (40h)	1273K (20h)
M=Zn	1023K (20h)	1473K (20h)
M=Ni	973K (40h)	1373K (20h)
M=Mg	1073K (20h)	1573K (20h)
$\text{Cs}_{0.9}\text{Al}_{0.9}\text{Si}_{2.1}\text{O}_6$	873K (24h)	1673K (10h)
$\text{Cs}_{0.875}\text{Rb}_{0.125}\text{AlSi}_2\text{O}_6$	873K (24h)	1673K (10h)
$\text{RbAlSi}_2\text{O}_6$	873K (24h)	
$\text{Rb}_{0.9}\text{Al}_{0.9}\text{Si}_{2.1}\text{O}_6$	873K (24h) 1273K (50h)	1623K (10h)
$\text{Rb}_{0.8}\text{Al}_{0.8}\text{Si}_{2.2}\text{O}_6$	873K (24h) 1273K (50h)	1673K (10h)

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

Sample	Chemical composition
$\text{CsBSi}_2\text{O}_6$	$\text{Cs}_{0.99(1)}\text{B}_{0.98(1)}\text{Si}_{2.00}\text{O}_6$
$\text{CsAlSi}_2\text{O}_6$	$\text{Cs}_{0.99(4)}\text{Al}_{0.98(1)}\text{Si}_{2.00}\text{O}_6$
$\text{CsFeSi}_2\text{O}_6$	$\text{Cs}_{1.00(1)}\text{Fe}_{0.99(1)}\text{Si}_{2.00}\text{O}_6$
$\text{CsB}_{0.2}\text{Al}_{0.8}\text{Si}_2\text{O}_6$	$\text{Cs}_{0.14(1)}\text{Al}_{0.83(1)}\text{Si}_{2.00}\text{O}_6$
$\text{CsAl}_{0.5}\text{Fe}_{0.5}\text{Si}_2\text{O}_6$	$\text{Cs}_{1.00(1)}\text{Al}_{0.46(1)}\text{Fe}_{0.54(1)}\text{Si}_{2.00}\text{O}_6$
$\text{CsAl}_{0.2}\text{Fe}_{0.8}\text{Si}_2\text{O}_6$	$\text{Cs}_{1.00(1)}\text{Al}_{0.20(1)}\text{Fe}_{0.81(1)}\text{Si}_{2.00}\text{O}_6$
$\text{Cs}_2\text{CdSi}_5\text{O}_{12}$	$\text{Cs}_{2.00(4)}\text{Cd}_{1.00(1)}\text{Si}_{5.00}\text{O}_{12}$
$\text{Cs}_2\text{MgSi}_5\text{O}_{12}$	$\text{Cs}_{1.99(4)}\text{Mg}_{0.98(1)}\text{Si}_{5.00}\text{O}_{12}$
$\text{Cs}_2\text{ZnSi}_5\text{O}_{12}$	$\text{Cs}_{2.03(4)}\text{Zn}_{1.00(1)}\text{Si}_{5.00}\text{O}_{12}$
$\text{Cs}_2\text{NiSi}_5\text{O}_{12}$	$\text{Cs}_{2.03(4)}\text{Ni}_{1.00(1)}\text{Si}_{5.00}\text{O}_{12}$
$\text{Cs}_{0.9}\text{Al}_{0.9}\text{Si}_{2.1}\text{O}_6$	$\text{Cs}_{0.88(4)}\text{Al}_{0.86(1)}\text{Si}_{2.10}\text{O}_6$
$\text{Cs}_{0.875}\text{Rb}_{0.125}\text{AlSi}_2\text{O}_6$	$\text{Cs}_{0.84(4)}\text{Rb}_{0.11(2)}\text{Al}_{0.94(1)}\text{Si}_{2.00}\text{O}_6$
$\text{RbAlSi}_2\text{O}_6$	$\text{Rb}_{1.01(1)}\text{Al}_{0.96(1)}\text{Si}_{2.00}\text{O}_6$
$\text{Rb}_{0.9}\text{Al}_{0.9}\text{Si}_{2.1}\text{O}_6$	$\text{Rb}_{0.90(1)}\text{Al}_{0.91(1)}\text{Si}_{2.10}\text{O}_6$
$\text{Rb}_{0.8}\text{Al}_{0.8}\text{Si}_{2.2}\text{O}_6$	$\text{Rb}_{0.83(1)}\text{Al}_{0.81(1)}\text{Si}_{2.20}\text{O}_6$

## 3. Results and discussion

### 3.1 Thermal expansion property of cubic $\text{CsMSi}_2\text{O}_6$ with molar ratio of $\text{Si}/\text{M}=2$ ( $\text{M}=\text{B}, \text{B}_{0.2}\text{Al}_{0.8}, \text{Al}, \text{Al}_{0.5}\text{Fe}_{0.5}, \text{Al}_{0.2}\text{Fe}_{0.8}, \text{Fe}$ )

There was a small difference between the intensities of each diffraction line in the XRD pattern at 298 K for synthetic cubic  $\text{CsMSi}_2\text{O}_6$  ( $\text{M}=\text{B}, \text{B}_{0.2}\text{Al}_{0.8}, \text{Al}, \text{Al}_{0.5}\text{Fe}_{0.5}, \text{Al}_{0.2}\text{Fe}_{0.8}, \text{Fe}$ ). Synthetic  $\text{CsMSi}_2\text{O}_6$  ( $\text{M}=\text{B}, \text{B}_{0.2}\text{Al}_{0.8}, \text{Al}, \text{Al}_{0.5}\text{Fe}_{0.5}, \text{Al}_{0.2}\text{Fe}_{0.8}, \text{Fe}$ ) was identified to be cubic with the space group  $Ia\bar{3}d$ , upon comparison with the XRD pattern of synthetic cubic  $\text{CsMSi}_2\text{O}_6$  ( $\text{M}=\text{B}, \text{Al}, \text{Fe}$ ). Cubic Cs-leucite compounds with molar ratios of more than  $\text{Al}/\text{B}=4$  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  $\text{CsMSi}_2\text{O}_6$  ( $\text{M}=\text{B}_{0.2}\text{Al}_{0.8}, \text{Al}_{0.5}\text{Fe}_{0.5}, \text{Al}_{0.2}\text{Fe}_{0.8}$ ) at 298–1073 K compared with that of cubic  $\text{CsMSi}_2\text{O}_6$  ( $\text{M}=\text{B}, \text{Al}, \text{Fe}$ ) represented by the dashed line. The thermal expansion property of the cubic  $\text{CsMSi}_2\text{O}_6$  ( $\text{M}=\text{B}, \text{Al}, \text{Fe}$ ) was identical to that in a previous report.<sup>3)</sup> Cubic  $\text{CsAl}_{0.2}\text{Fe}_{0.8}\text{Si}_2\text{O}_6$ , having  $\text{Al}_{0.2}\text{Fe}_{0.8}$  substituted for Fe in the M site of  $(\text{Si}, \text{M})\text{O}_4$

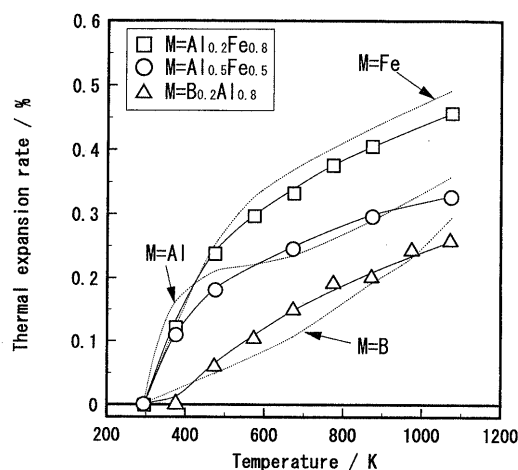


Fig. 1. Thermal expansion property of cubic  $\text{CsMSi}_2\text{O}_6$  ( $\text{M}=\text{B}_{0.2}\text{Al}_{0.8}, \text{Al}_{0.5}\text{Fe}_{0.5}, \text{Al}_{0.2}\text{Fe}_{0.8}$ ).

tetrahedra of cubic  $\text{CsFeSi}_2\text{O}_6$ , had a lower thermal expansion rate than that of cubic  $\text{CsFeSi}_2\text{O}_6$ . The thermal expansion rate of cubic  $\text{CsAl}_{0.5}\text{Fe}_{0.5}\text{Si}_2\text{O}_6$ , with  $\text{Al}_{0.5}\text{Fe}_{0.5}$  substituted for Al in the M site of  $(\text{Si}, \text{M})\text{O}_4$  tetrahedra for cubic  $\text{CsAlSi}_2\text{O}_6$ , was similar to that of cubic  $\text{CsAlSi}_2\text{O}_6$ . However, the lower thermal expansion property of cubic  $\text{CsAlSi}_2\text{O}_6$  in the range from 473 to 773 K was not recognized in cubic  $\text{CsAl}_{0.5}\text{Fe}_{0.5}\text{Si}_2\text{O}_6$ . On the other hand, cubic  $\text{CsMSi}_2\text{O}_6$  ( $\text{M}=\text{B}_{0.2}\text{Al}_{0.8}$ ) with  $\text{B}_{0.2}\text{Al}_{0.8}$  substituted for Al in the M site of  $(\text{Si}, \text{M})\text{O}_4$  tetrahedra of cubic  $\text{CsAlSi}_2\text{O}_6$  had a lower thermal expansion rate than cubic  $\text{CsAlSi}_2\text{O}_6$ , and the thermal expansion rate of cubic  $\text{CsMSi}_2\text{O}_6$  ( $\text{M}=\text{B}_{0.2}\text{Al}_{0.8}$ ) was similar to that of cubic  $\text{CsBSi}_2\text{O}_6$ .

On the basis of the above-mentioned results, it was found that the substitution of B for Al of the Al site for the  $(\text{Si}, \text{Al})\text{O}_4$  tetrahedra of cubic  $\text{CsAlSi}_2\text{O}_6$  or Al for Fe of the Fe site for the  $(\text{Si}, \text{Fe})\text{O}_4$  tetrahedra of cubic  $\text{CsFeSi}_2\text{O}_6$  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  $(\text{Si}, \text{M})\text{O}_4$  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  $(\text{Si}, \text{M})\text{O}_4$  tetrahedra of the framework structure.

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

Although there was a difference between the intensities of the diffraction lines in the XRD pattern for synthetic  $\text{Cs}_2\text{MSi}_5\text{O}_{12}$  ( $\text{M}=\text{Cd}, \text{Mg}, \text{Ni}, \text{Zn}$ ) and cubic  $\text{CsMSi}_2\text{O}_6$  ( $\text{M}=\text{B}, \text{Al}, \text{Fe}$ ), synthetic  $\text{Cs}_2\text{MSi}_5\text{O}_{12}$  ( $\text{M}=\text{Cd}, \text{Mg}, \text{Ni}, \text{Zn}$ ) was clearly cubic with the space group  $Ia\bar{3}d$ , based on the diffraction lines of its XRD patterns in comparison with those of cubic  $\text{CsMSi}_2\text{O}_6$  ( $\text{M}=\text{B}, \text{Al}, \text{Fe}$ ) with the space group  $Ia\bar{3}d$ .

Figure 2 shows the thermal expansion property of cubic  $\text{Cs}_2\text{MSi}_5\text{O}_{12}$  ( $\text{M}=\text{Cd}, \text{Mg}, \text{Ni}, \text{Zn}$ ) 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  $\text{CsMSi}_2\text{O}_6$  ( $\text{M}=\text{Al}, \text{Fe}$ ). The thermal expansion properties were differed, but the difference between the properties was not so great as in the case of the cubic  $\text{CsMSi}_2\text{O}_6$ . 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  $(\text{Si}, \text{M})\text{O}_4$  tetrahedra of the

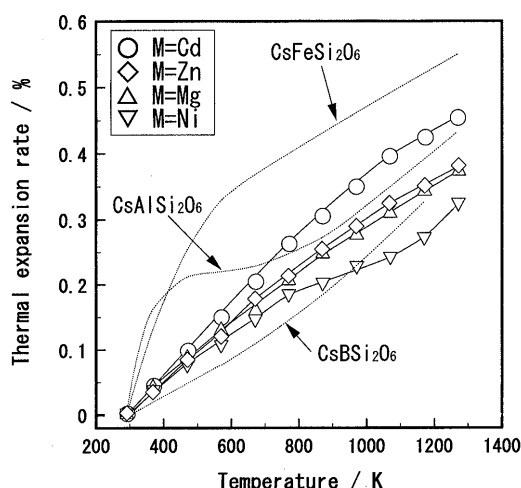


Fig. 2. Thermal expansion property of cubic  $\text{Cs}_2\text{MSi}_5\text{O}_{12}$  ( $\text{M}=\text{Cd}, \text{Mg}, \text{Ni}, \text{Zn}$ ).

framework structure. Moreover, because the lower thermal expansion rate of cubic  $\text{Cs}_2\text{NiSi}_5\text{O}_{12}$  in the range from 773–973 K is similar to that of cubic  $\text{CsAlSi}_2\text{O}_6$  in the range from 473–773 K, the lower thermal expansion property of cubic  $\text{CsAlSi}_2\text{O}_6$  is not a unique property.

Cubic  $\text{CsMSi}_2\text{O}_6$  ( $\text{M}=\text{B}, \text{Al}, \text{Fe}$ ) at 298 K has the lattice constants of  $a=1.2991$  nm for  $\text{M}=\text{B}$ ,  $a=1.3680$  nm for  $\text{M}=\text{Al}$ , and  $a=1.3840$  nm for  $\text{M}=\text{Fe}$ . On the other hand, cubic  $\text{Cs}_2\text{MSi}_5\text{O}_{12}$  ( $\text{M}=\text{Cd}, \text{Mg}, \text{Ni}, \text{Zn}$ ) at 298 K has the lattice constants of  $a=1.3780$  nm for  $\text{M}=\text{Cd}$ ,  $a=1.3679$  nm for  $\text{M}=\text{Mg}$ ,  $a=1.3640$  nm for  $\text{M}=\text{Ni}$  and  $a=1.3658$  nm for  $\text{M}=\text{Zn}$ . The relationship between the lattice constant and the ionic radius<sup>9)</sup> of M of the  $(\text{M}, \text{Si})\text{O}_4$  tetrahedra for the synthetic cubic Cs-leucite compound with the space group  $Ia\bar{3}d$  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  $(\text{Si}, \text{M})\text{O}_4$  tetrahedra of  $\text{CsMSi}_2\text{O}_6$  ( $\text{M}=\text{Al}, \text{Fe}$ ) was 2 and that of  $\text{Cs}_2\text{MSi}_5\text{O}_{12}$  ( $\text{M}=\text{Cd}, \text{Mg}, \text{Ni}, \text{Zn}$ ) was 5, it was found that the increase of the Si/M molar ratio of  $(\text{Si}, \text{M})\text{O}_4$  tetrahedra was effective in decreasing the thermal expansion rate of the cubic Cs-leucite compounds.

### 3.3 Thermal expansion property of cubic $\text{Cs}_{0.9}\text{Al}_{0.9}\text{Si}_{2.1}\text{O}_6$ with vacant Cs site

The crystalline system of synthetic  $\text{Cs}_{0.9}\text{Al}_{0.9}\text{Si}_{2.1}\text{O}_6$  was considered to be cubic with the space group  $Ia\bar{3}d$  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  $\text{Cs}_{0.9}\text{Al}_{0.9}\text{Si}_{2.1}\text{O}_6$  only decreased with increasing temperature due to thermal expansion without a structural phase transition, synthetic  $\text{Cs}_{0.9}\text{Al}_{0.9}\text{Si}_{2.1}\text{O}_6$  was recognized to be cubic with the space group  $Ia\bar{3}d$  above 298 K.

The thermal expansion property of cubic  $\text{Cs}_{0.9}\text{Al}_{0.9}\text{Si}_{2.1}\text{O}_6$  in the range from 298–1273 K was investigated by HTXRD and the results are shown with those of cubic  $\text{CsAlSi}_2\text{O}_6$  in Fig. 4. Cubic  $\text{CsAlSi}_2\text{O}_6$  and  $\text{Cs}_{0.9}\text{Al}_{0.9}\text{Si}_{2.1}\text{O}_6$  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  $\text{Cs}_{0.9}\text{Al}_{0.9}\text{Si}_{2.1}\text{O}_6$  in the range from 298–1273 K was lower than that of cubic  $\text{CsAlSi}_2\text{O}_6$ . It was considered that the lower thermal expansion property of cubic  $\text{Cs}_{0.9}\text{Al}_{0.9}\text{Si}_{2.1}\text{O}_6$  above 298 K was due to the shift of the temperature range of the larger thermal expansion proper-

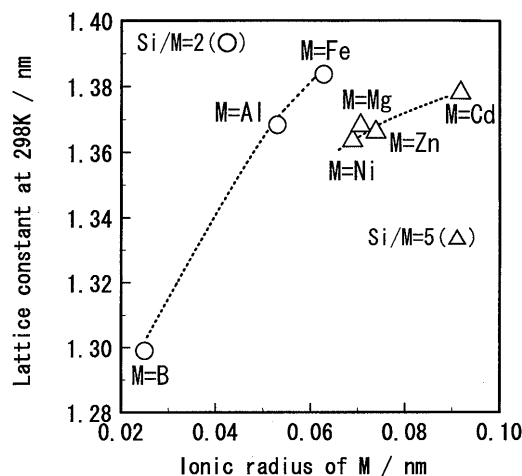
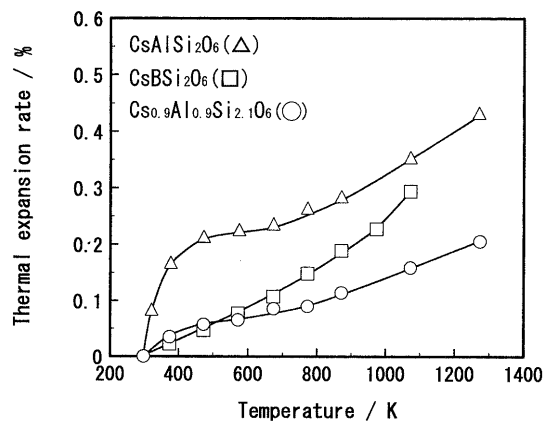
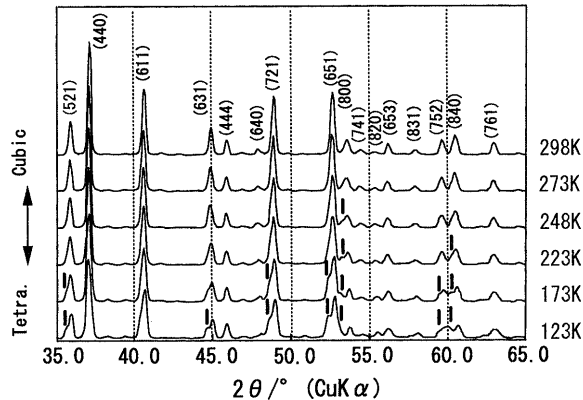
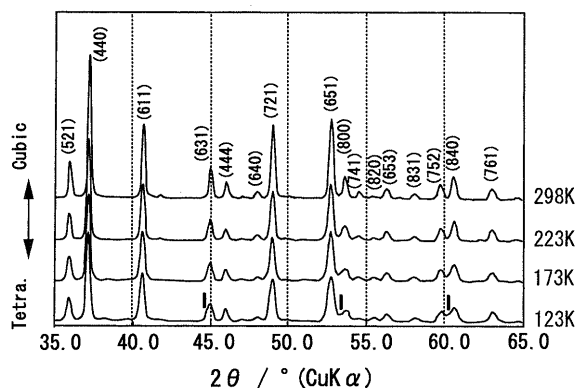
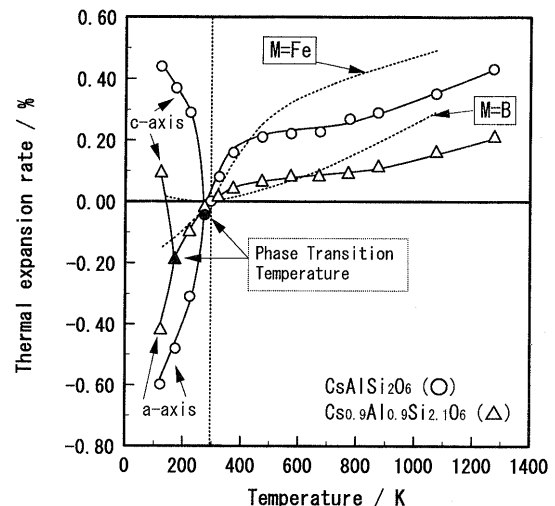


Fig. 3. Effect of ionic radius of M cation on lattice constant of leucite-type compound at 298 K.

Fig. 4. Thermal expansion property of cubic  $\text{Cs}_{0.9}\text{Al}_{0.9}\text{Si}_{2.1}\text{O}_6$ .

ty to a lower temperature range. On the other hand, the temperature range of that of cubic  $\text{CsAlSi}_2\text{O}_6$  was from 298 to 473 K.

The XRD patterns of  $\text{CsAlSi}_2\text{O}_6$  and  $\text{Cs}_{0.9}\text{Al}_{0.9}\text{Si}_{2.1}\text{O}_6$  in the range from 123–298 K were investigated by LTXRD. The results are shown in Figs. 5 and 6. The diffraction lines of  $\text{CsAlSi}_2\text{O}_6$  were split below 248 K, while the diffraction lines of  $\text{Cs}_{0.9}\text{Al}_{0.9}\text{Si}_{2.1}\text{O}_6$  were split below 173 K, which is about 75 K lower than the temperature for  $\text{CsAlSi}_2\text{O}_6$ , and exhibited changes of the diffraction lines due to the structural phase transition from tetragonal to cubic<sup>7),10),11)</sup> with increasing temperature. Therefore, it was concluded

Fig. 5. Change of XRD pattern for  $\text{CsAlSi}_2\text{O}_6$  in the temperature range from 123 to 298 K.Fig. 6. Change of XRD pattern for  $\text{Cs}_{0.9}\text{Al}_{0.9}\text{Si}_{2.1}\text{O}_6$  in the temperature range from 123 to 298 K.Fig. 7. Thermal expansion properties of  $\text{CsMSi}_2\text{O}_6$  ( $M=\text{B}, \text{Fe}$ ) and  $\text{Cs}_{0.9}\text{Al}_{0.9}\text{Si}_{2.1}\text{O}_6$ .

that  $\text{CsAlSi}_2\text{O}_6$  and  $\text{Cs}_{0.9}\text{Al}_{0.9}\text{Si}_{2.1}\text{O}_6$  undergo a structural phase transition from tetragonal to cubic, and that the structural phase transition temperatures are around 248 K and 173 K, respectively.

As shown in Fig. 7, the lattice constant for tetragonal  $\text{CsAlSi}_2\text{O}_6$  of the  $a$ -axis increased and that of the  $c$ -axis decreased with increasing temperature from 123 to 273 K. Consequently, cubic  $\text{CsAlSi}_2\text{O}_6$  showed a larger thermal expansion at 273–473 K. Tetragonal  $\text{Cs}_{0.9}\text{Al}_{0.9}\text{Si}_{2.1}\text{O}_6$  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  $\text{Cs}_{0.9}\text{Al}_{0.9}\text{Si}_{2.1}\text{O}_6$  showed the larger thermal expansion in the range from 173–323 K after undergoing the structural phase transition. The mean linear thermal expansion coefficient of cubic  $\text{Cs}_{0.9}\text{Al}_{0.9}\text{Si}_{2.1}\text{O}_6$  in the range from 298–1273 K was  $2.05 \times 10^{-6}/\text{K}$ . In comparison with the mean linear thermal expansion coefficient of cubic  $\text{CsBSi}_2\text{O}_6$  of  $2.75 \times 10^{-6}/\text{K}$  in the range from 298–1073 K,<sup>3)</sup> it was suggested that cubic  $\text{Cs}_{0.9}\text{Al}_{0.9}\text{Si}_{2.1}\text{O}_6$  had a lower thermal expansion rate than that of cubic  $\text{CsBSi}_2\text{O}_6$  above 298 K, as shown in Fig. 4. The thermal expansion property of  $\text{Cs}_{0.9}\text{Al}_{0.9}\text{Si}_{2.1}\text{O}_6$  in the range from 123–1273 K was similar in shape to that of  $\text{CsAlSi}_2\text{O}_6$  in the range from 298–1273 K. Therefore, it was considered that the lower thermal expansion property of cubic  $\text{Cs}_{0.9}\text{Al}_{0.9}\text{Si}_{2.1}\text{O}_6$  in the range from 298–1273 K was due to the structural phase transition temperature, which is about 75 K lower than that of  $\text{CsAlSi}_2\text{O}_6$ , in addition to the larger thermal expansion of  $\text{Cs}_{0.9}\text{Al}_{0.9}\text{Si}_{2.1}\text{O}_6$ . On the other hand, synthetic  $\text{CsMSi}_2\text{O}_6$  ( $M=\text{B}, \text{Fe}$ ) did not undergo a structural phase transition, even at a lower temperature.

The lattice constants of synthetic  $\text{RbAlSi}_2\text{O}_6$ ,  $\text{Rb}_{0.9}\text{Al}_{0.9}\text{Si}_{2.1}\text{O}_6$  and  $\text{Rb}_{0.8}\text{Al}_{0.8}\text{Si}_{2.2}\text{O}_6$  in the temperature range from 298 to 1273 K are shown in Fig. 8. The crystalline systems of  $\text{Rb}_{0.9}\text{Al}_{0.9}\text{Si}_{2.1}\text{O}_6$  and  $\text{Rb}_{0.8}\text{Al}_{0.8}\text{Si}_{2.2}\text{O}_6$  were found to be tetragonal with the space group  $I4_1/a$  at 298 K upon comparison with the XRD pattern of tetragonal  $\text{RbAlSi}_2\text{O}_6$ . The lattice constants of the  $a$ -axis increased and those of the  $c$ -axis decreased with increasing temperature, as did those of tetragonal  $\text{RbAlSi}_2\text{O}_6$  and tetragonal  $\text{Cs-leucites}$ . The structural phase transition temperature decreased with decreasing number of  $\text{Rb}^+$  ions of  $\text{Rb-leucites}$ , and also the thermal expansion rate of cubic  $\text{Rb-leucite}$  in the range from 673–1273 K decreased with decreasing number of  $\text{Rb}^+$  ions of  $\text{Rb-leucite}$ . On the basis of the above-mentioned result, it was concluded that the tendency for the decrease of the

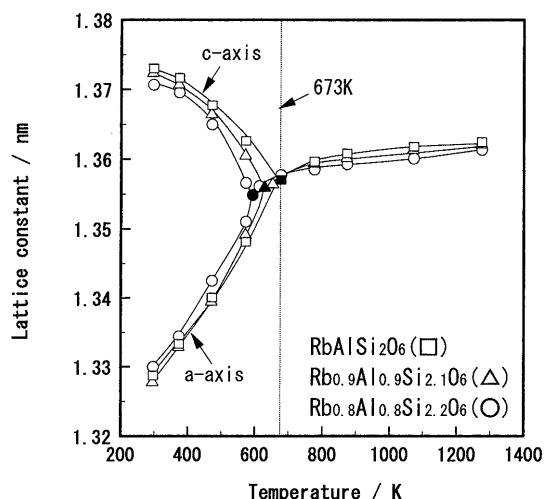


Fig. 8. Lattice constants of synthesized  $\text{RbAlSi}_2\text{O}_6$ ,  $\text{Rb}_{0.9}\text{Al}_{0.9}\text{Si}_{2.1}\text{O}_6$  and  $\text{Rb}_{0.8}\text{Al}_{0.8}\text{Si}_{2.2}\text{O}_6$  in the temperature range from 298 to 1273 K. Solid plots show the phase transition temperature of Rb-leucite.

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  $\text{CsAlSi}_2\text{O}_6$ ,  $\text{Cs}_{0.9}\text{Al}_{0.9}\text{Si}_{2.1}\text{O}_6$ , and  $\text{Cs}_{7/8}\text{Rb}_{1/8}\text{AlSi}_2\text{O}_6$  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  $\text{Cs}_{7/8}\text{Rb}_{1/8}\text{AlSi}_2\text{O}_6$  at 298 K was smaller than that of  $a=1.3682$  nm for cubic  $\text{CsAlSi}_2\text{O}_6$ . This was because the unit cell of cubic  $\text{Cs}_{7/8}\text{Rb}_{1/8}\text{AlSi}_2\text{O}_6$  had  $\text{Rb}^+$  ions replaced with 12.5 mol% of  $\text{Cs}^+$  ions in the unit cell of cubic  $\text{CsAlSi}_2\text{O}_6$ . On the other hand, the lattice constant of  $a=1.3679$  nm for cubic  $\text{Cs}_{0.9}\text{Al}_{0.9}\text{Si}_{2.1}\text{O}_6$  with Cs vacant sites replaced with 10 mol% of  $\text{Cs}^+$  ions in the unit cell of cubic  $\text{CsAlSi}_2\text{O}_6$  was almost the same as that of cubic  $\text{CsAlSi}_2\text{O}_6$  without decreasing lattice constant at 298 K.

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

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  $\text{CsMSi}_2\text{O}_6$  ( $M=\text{B}, \text{Al}, \text{Fe}, \text{B}_{0.2}$

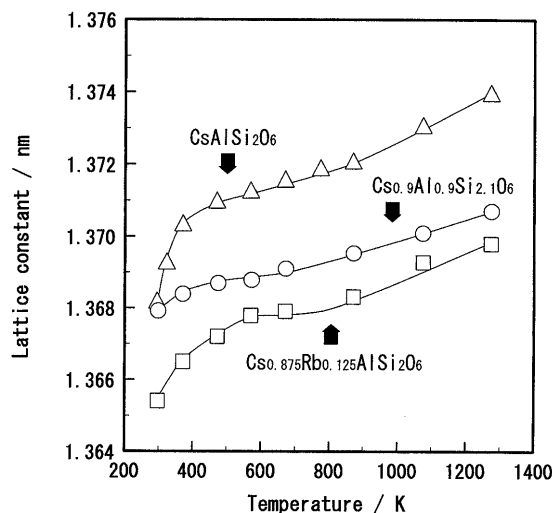


Fig. 9. Lattice constant of cubic leucite-type compound in the temperature range from 298 to 1273 K.

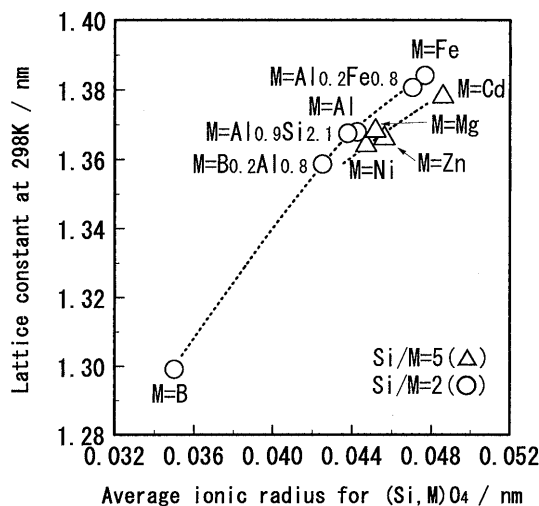


Fig. 10. Relationship between average ionic radius of M cation and lattice constants of cubic leucite-type compounds.

$\text{Al}_{0.8}$ ,  $\text{Al}_{0.2}\text{Fe}_{0.8}$ ) and  $\text{Cs}_{0.9}\text{Al}_{0.9}\text{Si}_{2.1}\text{O}_6$ , or Eq. (2) for  $\text{Cs}_2\text{MSi}_5\text{O}_{12}$  ( $M=\text{Ni}, \text{Mg}, \text{Zn}, \text{Cd}$ ).

$$\begin{aligned} \text{Average ionic radius} &= \{(\text{Ionic radius of } ^{\text{IV}}\text{Si}^{4+} \text{ ion}) \times 2 \\ &+ (\text{Ionic radius of } ^{\text{IV}}\text{M}^{3+} \text{ ion})\} / 3 \end{aligned} \quad (1)$$

$$\begin{aligned} \text{Average ionic radius} &= \{(\text{Ionic radius of } ^{\text{IV}}\text{Si}^{4+} \text{ ion}) \times 5 \\ &+ (\text{Ionic radius of } ^{\text{IV}}\text{M}^{2+} \text{ ion})\} / 6 \end{aligned} \quad (2)$$

Here, IV is the coordination number. The lattice constant was found to increase with increasing average ionic radius for the  $(\text{Si}, \text{M})\text{O}_4$  tetrahedra. In view of the relationship between average ionic radius and the lattice constant, it is interesting that  $\text{Cs}_{0.9}\text{Al}_{0.9}\text{Si}_{2.1}\text{O}_6$  showed the lower thermal expansion rate mentioned above. The unit cell of  $\text{Cs}_{0.9}\text{Al}_{0.9}\text{Si}_{2.1}\text{O}_6$  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  $Ia\bar{3}d$  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-

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  $\text{CsB}_{0.2}\text{Al}_{0.8}\text{Si}_2\text{O}_6$  had a lower thermal expansion rate than cubic  $\text{CsAlSi}_2\text{O}_6$ , and also, both synthetic cubic  $\text{CsAl}_{0.5}\text{Fe}_{0.5}\text{Si}_2\text{O}_6$  and  $\text{CsAl}_{0.2}\text{Fe}_{0.8}\text{Si}_2\text{O}_6$  had lower thermal expansion rates than cubic  $\text{CsFeSi}_2\text{O}_6$ .

(2) Synthetic cubic  $\text{Cs}_2\text{MSi}_5\text{O}_{12}$  ( $M=\text{Cd, Mg, Ni, Zn}$ ) with the molar ratio of  $\text{Si}/M=5$  had a lower thermal expansion rate. This property of  $\text{Cs}_2\text{MSi}_5\text{O}_{12}$  ( $M=\text{Cd, Mg, Ni, Zn}$ ) was clearly different from that of  $\text{CsMSi}_2\text{O}_6$  ( $M=\text{B, Al, Fe}$ ) with the molar ratio of  $\text{Si}/M=2$ , 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  $\text{Cs}_{0.9}\text{Al}_{0.9}\text{Si}_{2.1}\text{O}_6$  showed a lower thermal expansion than synthetic cubic  $\text{CsAlSi}_2\text{O}_6$ , and had the mean linear thermal expansion coefficient of  $2.05 \times 10^{-6}/\text{K}$  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  $\text{Si}/M$  of the  $(\text{Si, M})\text{O}_4$  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*.

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