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THERMAL PROPERTY AND PHASE TRANSITION OF THE SYNTHESIZED NEW CUBIC LEUCITE-TYPE COMPOUNDS

I. Yanase[1], *H. Kobayashi*[1] *and T. Mitamura*[2]

[1]Department of Applied Chemistry, Faculty of Engineering, Saitama University
255 Shimoohkubo, Urawa, 338-8570
[2]Graduate School, Saitama Institute of Technology, 1690 Fusaiji, Okabe-machi, Ohsato-gun
Saitama, 369-0293 Japan

Abstract

New cubic leucite-type compounds, $CsMSi_2O_6$ (M=$B_{0.2}Al_{0.8}$,$Al_{0.2}Fe_{0.8}$), $Cs_2MSi_5O_{12}$ (M=Cd, Mg, Ni, Zn) have been synthesized by the two-stage heat treatment of the solid-state reaction. The thermal expansion properties of the synthesized leucite-type compounds have been studied with HTXRD and LTXRD in the temperature range of 123 to 1273 K. The thermal expansion rate of $CsB_{0.2}Al_{0.8}Si_2O_6$ was found to be considerably smaller than that of $CsAlSi_2O_6$, while the thermal expansion property of $Cs_2MSi_5O_{12}$ (M=Mg, Zn, Cd) was found to have a linear relationship in the temperature range of 298 to 1273 K. By using Rietveld analysis it was found that the thermal expansion rate decreased with increasing the Si–O–M(Si) angle for cubic leucite-type compounds at 298 K, and that the phase transitions of $CsAlSi_2O_6$ and $Cs_{0.9}Al_{0.9}Si_{2.1}O_6$ were due to the relationship between the bond angle of Si–O–M(Si) of the three-dimensional framework structure and the space ratio in the unit cell at 298 K.

Keywords: crystal angle, leucite, phase transition, thermal expansion

Introduction

Fused silica (SiO_2), cordierite ($Mg_2Al_4Si_5O_{18}$), and β-spodumene ($LiAlSi_2O_6$) were known as the lower thermal expansion materials. However, cubic silicate compounds have not been studied as the lower thermal expansion materials.

Cubic $CsMSi_2O_6$ (M=B, Al, Fe) with space group Ia-3d and tetragonal $MAlSi_2O_6$ (M=K, Rb) with space group $I4_1/a$ have a three-dimensional aluminosilicate framework structure composed of 32 SiO_4 tetrahedra and 16 MO_4 tetrahedra with 16 alkaline cations occupying large 12-coordinate cavities in the unit cell [1–3]. The thermal expansion properties of cubic $CsBSi_2O_6$, $CsAlSi_2O_6$, and $CsFeSi_2O_6$ were known to be different from each other [3]. The thermal expansion rates decreased with increasing ionic radius of M^{3+} ion.

$KAlSi_2O_6$ and $RbAlSi_2O_6$ [4–6] undergo the phase transition of tetragonal to cubic in the temperature ranges of 873 to 913 and of 583 to 673 K, respectively, while $CsAlSi_2O_6$ is cubic above 298 K and has undergone the phase transition at about

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273 K [7]. The mean linear thermal expansion coefficient of $CsAlSi_2O_6$ is about $10\cdot10^{-6}$/K in the temperature range of 298 to 473 K, and that of $CsAlSi_2O_6$ is about $2.2\cdot10^{-6}$/K in the temperature range of 473 to 1273 K [3, 7, 8].

In this work, various new cubic leucite-type compounds, $CsMSi_2O_6$ (M=$B_{0.2}Al_{0.8}$, $Al_{0.2}Fe_{0.8}$), $Cs_2MSi_5O_{12}$ (M=Cd, Mg, Ni, Zn), and $CsMSi_2O_6$ (M=B, Al, Fe) have been prepared by the two-stage heat treatment of the solid-state reaction [8, 9], and then the thermal expansion properties, which have not been reported excluding $CsMSi_2O_6$ (M=B, Al, Fe), have been studied. Also, the relationship between the thermal expansion property and the phase transition of tetragonal to cubic for the synthesized leucite-type compounds have been investigated from the viewpoint of the crystal structure.

Experimental

Synthesis of leucite-type compounds with cubic symmetry

Synthesis of $CsMSi_2O_6$ (M=B, Al, Fe, $B_{0.2}Al_{0.8}$, $Al_{0\cdot2}Fe_{0.8}$)

The single phases of $CsMSi_2O_6$ (M=B, Al, Fe, $B_{0.2}Al_{0.8}$, $Al_{0.2}Fe_{0.8}$) and $Cs_{0.9}Al_{0.9}Si_{2.1}O_6$ were synthesized by the two-stage heat treatment [8] of the mixed powder of $CsNO_3$, SiO_2(α-quartz) and H_3BO_3, γ-Al_2O_3 and Fe_2O_3, which was given as molar ratios of Cs/M=1.0/1.0, M/Si=1.0/2.0, and Al/Si=0.9/2.1 for $Cs_{0.9}Al_{0.9}Si_{2.1}O_6$. The mixed powders were calcined in an Al_2O_3 crucible at 873 to 973 K for 24 h in air, and then the calcined powder were heated at 1173 to 1673 K for 2 to 10 h in air [8].

Synthesis of $Cs_2MSi_5O_{12}$ (M=Cd, Mg, Ni, Zn)

The single phases of $Cs_2MSi_5O_{12}$ (M=Cd, Mg, Ni, Zn) were synthesized by the two-stage heat treatment [9] of the mixed powder of $CsNO_3$, SiO_2(α-quartz) and MO (M=Cd, Mg, Ni, Zn), which was given as molar ratios of Cs/M=2.0/1.0 and M/Si=1.0/5.0. The mixed powders were calcined at 973 to 1073 K for 20 to 40 h in air until the cubic $Cs_2MSi_5O_{12}$ (M=Cd, Mg, Ni, Zn) phase with space group Ia-3d was identified with XRD, and then they were heated at 1273 to 1573 K for 20 h in air [9].

Thermal expansion property of the synthesized leucite-type compounds

Thermal expansion properties, upon heating, of the synthesized leucite-type compounds were investigated in the viewpoint of the change of the lattice constants with temperatures. The lattice constants of the synthesized leucite-type compounds in the temperature ranges of 123 to 298 K and 298 to 1273 K were examined by low-temperature X-ray diffraction (LTXRD; MXP18VA equipped with monochrometer, CuK_α, 40 kV, 200 mA, MAC Science, Yokohama, Japan) and high-temperature X-ray diffraction (HTXRD; MXP18VA equipped with monochrometer, CuK_α, 40 kV, 200 mA, MAC Science, Yokohama, Japan), respectively.

The lattice constants of cubic leucite-type compounds with temperatures were calculated, followed by holding the sample for five minutes, from the 2θ value by the least-squares method with the six peaks of (332),(440),(532),(631),(721) and (732) planes appearing at a 2θ of 25 to 55°, which were corrected using Si as the external standard at the scanning speed of $1^\circ\,\mathrm{min}^{-1}$ in the temperature range of 298 to 1273 K. Measuring sample was set in a Pt holder contacting with a thermocouple.

Rietveld analysis

XRD patterns of the synthesized leucite-type compounds were obtained by the FT method (CuK_α, 40 kV, 200 mA, fixed time: 1 s, step: 0.03) and the fractional coordinates for the synthesized leucite-type compounds were refined with the Rietveld analysis (software: RIETAN94) [10, 11] for the XRD patterns at 298 K.

Results and discussion

Thermal expansion property of the synthesized $CsMSi_2O_6$ (M=B, Al, Fe, $B_{0.2}Al_{0.8}$, $Al_{0.2}Fe_{0.8}$) and $Cs_2MSi_5O_{12}$ (M=Ni, Zn, Mg, Cd)

The synthesized leucite-type compounds, $\mathrm{CsMSi_2O_6}$ (*M*=B, Al, Fe, $\mathrm{B_{0.2}Al_{0.8}}$, $\mathrm{Al_{0.2}Fe_{0.8}}$) and $\mathrm{Cs_2MSi_5O_{12}}$ (*M*=Ni, Zn, Mg, Cd), were considered as cubic with space group Ia-3d from the measured XRD patterns at 298 K, and Fig. 1 shows the XRD patterns of the synthesized $\mathrm{Cs_2MSi_5O_{12}}$ (*M*=Ni, Zn, Mg, Cd) at 298 K. The change of lattice constants of the synthesized leucite-type compound was investigated in the temperature range of 298 to 1273 K by using HTXRD. 2θ angles for each diffraction line of cubic leucite-type compounds decreased with increasing temperature due to the thermal expansion without phase transitions. From the results, the synthesized leucite-type compounds were found to be cubic with space group Ia-3d above 298 K.

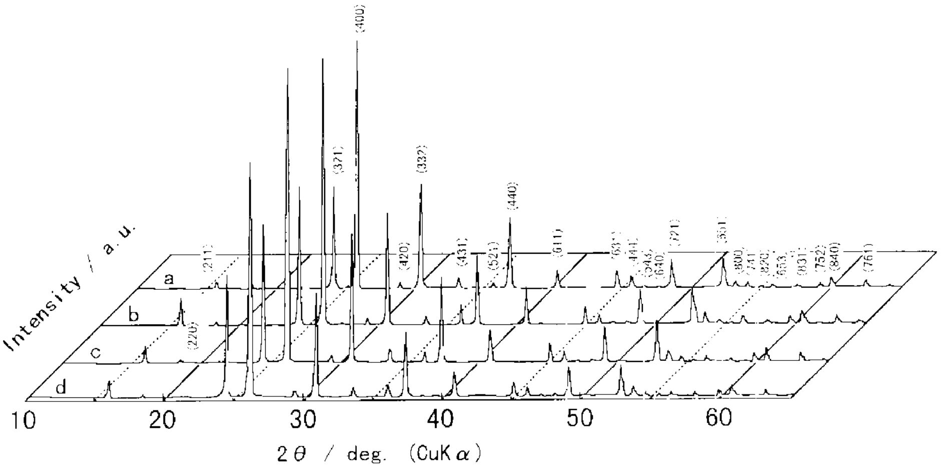

Fig. 1 XRD patterns of the synthesized $\mathrm{Cs_2MSi_5O_{12}}$ (*M*=Cd, Mg, Ni, Zn) powder.
a – $\mathrm{Cs_2CdSi_5O_{12}}$, b – $\mathrm{Cs_2MgSi_5O_{12}}$, c – $\mathrm{Cs_2MZnSi_5O_{12}}$, d – $\mathrm{Cs_2NiSi_5O_{12}}$

The thermal expansion properties of the synthesized $CsMSi_2O_6$ (M=B, Al, Fe, $B_{0.2}Al_{0.8}$, $Al_{0.2}Fe_{0.8}$) in the temperature range of 298 to 1073 K were investigated and the results are shown in Fig. 2. At 298 K the synthesized $CsBSi_2O_6$, $CsAlSi_2O_6$ and

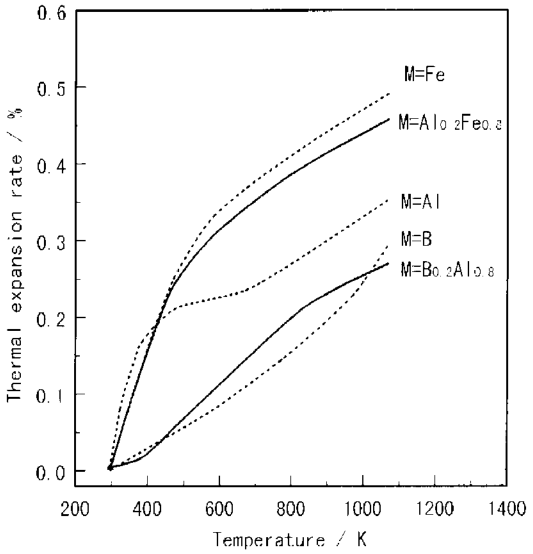

Fig. 2 Thermal expansion property of the synthesized $CsMSi_2O_6$ (M=B, Al, Fe, $B_{0.2}Al_{0.8}$, $Al_{0.2}Fe_{0.8}$) with cubic symmetry, space group Ia-3d, in the temperature range of 298 to 1073 K

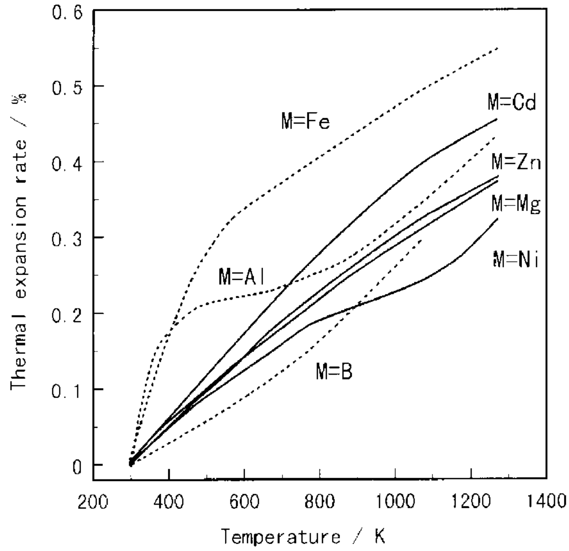

Fig. 3 Thermal expansion property of the synthesized $CsMSi_2O_6$ (M=B, Al, Fe) and $Cs_2MSi_5O_{12}$ (M=Ni, Mg, Zn, Cd) with cubic symmetry, space group Ia-3d, in the temperature range of 298 to 1273 K

$CsFeSi_2O_6$ had the lattice constants of *a*=1.2991, *a*=1.3682 and *a*=1.3834 nm, respectively. The lattice constant and the thermal expansion property of the synthesized $CsMSi_2O_6$ (*M*=B, Al, Fe) in the temperature range of 298 to 1073 K were almost similar to those reported [3, 7, 8]. The lattice constants of the synthesized $CsAl_{0.2}Fe_{0.8}Si_2O_6$ and $CsB_{0.2}Al_{0.8}Si_2O_6$ were *a*=1.3585 and *a*=1.3805 nm, respectively, at 298 K. The thermal expansion rate of the synthesized $CsAl_{0.2}Fe_{0.8}Si_2O_6$ was found to be slightly smaller than that of $CsFeSi_2O_6$ in the temperature range of 298 to 1273 K. On the other hand, the thermal expansion rate of the synthesized $CsB_{0.2}Al_{0.8}Si_2O_6$ was found to be considerably smaller than that of $CsAlSi_2O_6$.

The thermal expansion properties of the synthesized $Cs_2MSi_5O_{12}$ (*M*=Ni, Mg, Zn, Cd) in the temperature range of 298 to 1273 K were investigated and the results are shown in Fig. 3. At 298 K the synthesized $Cs_2NiSi_5O_{12}$, $Cs_2MgSi_5O_{12}$, $Cs_2ZnSi_5O_{12}$ and $Cs_2CdSi_5O_{12}$ had the lattice constants of *a*=1.3640, *a*=1.3679, *a*=1.3660 and *a*=1.3780 nm, respectively. It was found that the thermal expansion properties of the synthesized $Cs_2MSi_5O_{12}$ (*M*=Mg, Zn, Cd) showed a linear relationship in the temperature range of 298 to 1273 K, and $Cs_2NiSi_5O_{12}$ was similar to $CsAlSi_2O_6$.

Phase transition of the synthesized $CsAlSi_2O_6$ and $Cs_{0.9}Al_{0.9}Si_{2.1}O_6$

In the temperature range of 123 to 298 K, XRD patterns of the synthesized $CsAlSi_2O_6$ and $Cs_{0.9}Al_{0.9}Si_{2.1}O_6$ were investigated using LTXRD. The results are shown in Figs 4 and 5. The diffraction lines for the synthesized $CsAlSi_2O_6$ were split under 248 K. On the other hand, the diffraction lines of the synthesized $Cs_{0.9}Al_{0.9}Si_{2.1}O_6$ were split under 173 K, which is about 75 K lower than that of $CsAlSi_2O_6$. $KAlSi_2O_6$ and $RbAlSi_2O_6$, which were tetragonal system at 298 K, had the changes of the diffraction lines with increasing temperature by the phase transi-

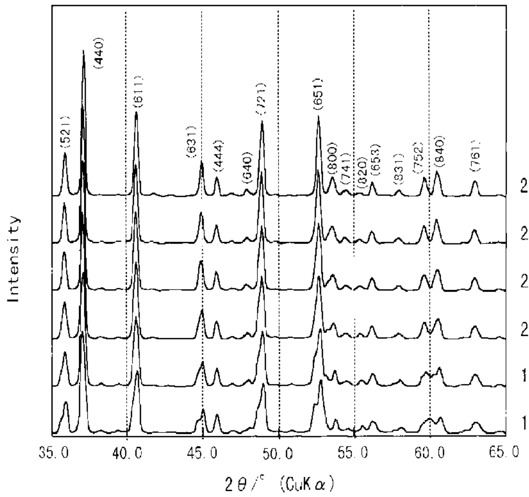

Fig. 4 Change of XRD pattern for $CsAlSi_2O_6$ in the temperature range of 123 to 298 K

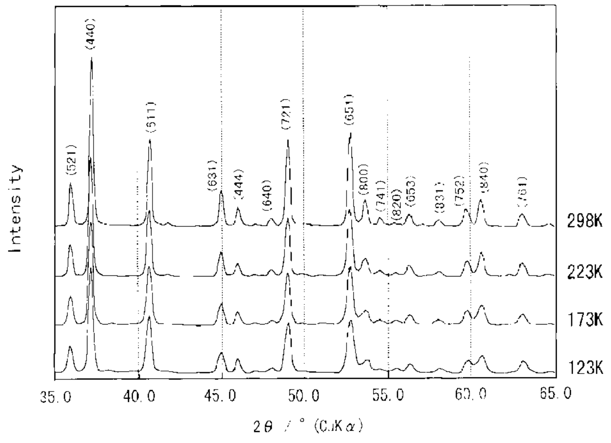

Fig. 5 Change of XRD pattern for $Cs_{0.9}Al_{0.9}Si_{2.1}O_6$ in the temperature range of 123 to 298 K

tion [4–6]. Therefore, it was found that the synthesized $CsAlSi_2O_6$ and $Cs_{0.9}Al_{0.9}Si_{2.1}O_6$ underwent a phase transition of tetragonal to cubic, and the phase transition temperature were 248 and 173 K, respectively.

In Fig. 6, $CsAlSi_2O_6$ showed that the lattice constant of a-axis increased and that of c-axis decreased with increasing temperature in the temperature range of 123 to 273 K, followed by the phase transition of tetragonal to cubic at 273 K, and then showed the large thermal expansion in the temperature range of 273 to 473 K. $Cs_{0.9}Al_{0.9}Si_{2.1}O_6$ also showed that the lattice constant of a-axis increased and that of c-axis decreased with increasing temperature in the temperature range of 123 to

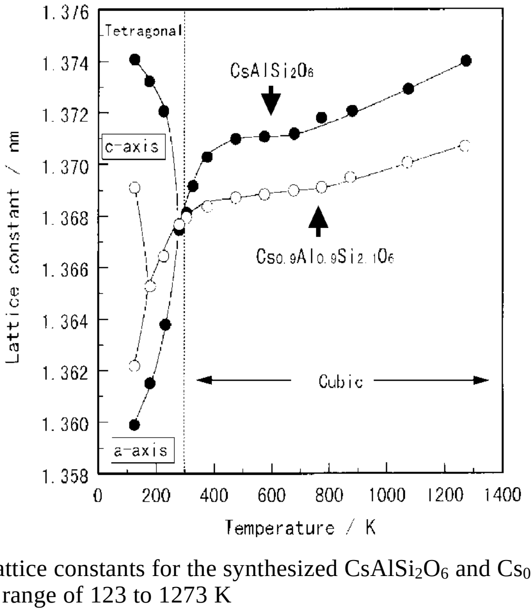

Fig. 6 Change of lattice constants for the synthesized $CsAlSi_2O_6$ and $Cs_{0.9}Al_{0.9}Si_{2.1}O_6$ in the temperature range of 123 to 1273 K

173 K, followed by the phase transition of tetragonal to cubic at 173 K and showed the large thermal expansion in the temperature range of 173 to 323 K. The mean linear thermal expansion coefficient of the synthesized $Cs_{0.9}Al_{0.9}Si_{2.1}O_6$ was $2.05\cdot10^{-6}$/K in the temperature range of 298 to 1273 K. $CsBSi_2O_6$ has been known as one of cubic leucite-type compounds having the lowest thermal expansion ($2.75\cdot10^{-6}$/K, *RT*~1073 K) above 298 K [3]. However, $Cs_{0.9}Al_{0.9}Si_{2.1}O_6$ had a lower thermal expansion rate than $CsBSi_2O_6$ above 298 K. A lower thermal expansion rate of $Cs_{0.9}Al_{0.9}Si_{2.1}O_6$ in the temperature range of 298 to 1273 K was due to the lower phase transition temperature about 75 K lower than that of the synthesized $CsAlSi_2O_6$ followed by the large thermal expansion. Therefore, it was found that decreasing the number of Cs^+ ions of $CsAlSi_2O_6$ was effective for decreasing the thermal expansion rate. The same effect was observed for the synthesized $RbAlSi_2O_6$, $Rb_{0.9}Al_{0.9}Si_{2.1}O_6$ and $Rb_{0.8}Al_{0.8}Si_{2.2}O_6$ in the temperature range of 673 to 1273 K [20].

In Fig. 7, the two solid lines showed the thermal expansion properties for the synthesized $CsBSi_2O_6$ and $CsFeSi_2O_6$ in the temperature range of 123 to 1273 K, respectively. The splitting of the diffraction lines for $CsBSi_2O_6$ and $CsFeSi_2O_6$ was not observed in the temperature range of 123 to 298 K. It was thought that the negative thermal expansion rate of $CsBSi_2O_6$ was due to the anisotropic thermal displacements of oxygen atoms in the unit cell, similar to α-quartz [21]. On the other hand, the thermal expansion rate of the synthesized $CsFeSi_2O_6$ in the temperature range of 123 to 298 K was larger than that of $CsBSi_2O_6$. By considering the size difference of tetrahedral cation in the unit cell of cubic leucite-type compound, it was suggested that the thermal expansion property for cubic leucite-type compounds were influenced by the framework in the unit cell.

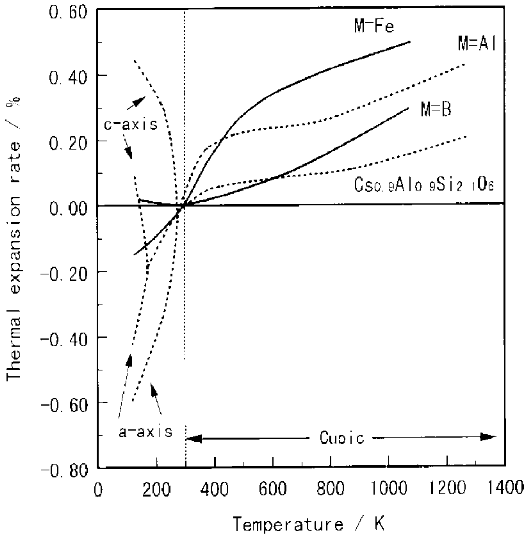

Fig. 7 Thermal expansion property of the synthesized $CsMSi_2O_6$ (*M*=B, Al, Fe) and $Cs_{0.9}Al_{0.9}Si_{2.1}O_6$ in the temperature range of 123 to 1273 K

Effective factor of thermal expansion property

Rietveld analysis [10, 11] was performed for the synthesized cubic leucite-type compounds at 298 K. The refined fractional coordinates and thermal isotropic displacement parameter (B) for $CsAlSi_2O_6$ are shown as an instance in Table 1. Crystal structure of the lower half of the unit cell for cubic leucite-type compounds with space group Ia-3d is shown in Fig 8. The bond angles between tetrahedal cations, Si or M (M=B, Al, Fe, Ni, Mg, Zn, Cd), and O were calculated at 298 K. It was considered the bond angles of Si–O–M(Si) influenced upon the lattice constants of the cubic leucite-type compounds. Figure 9 shows the relationship between the bond angle of Si–O–M(Si) and average radius [22] which was calculated by the Eq. (1) for $CsMSi_2O_6$ (M=B, Al, Fe, $B_{0.2}Al_{0.8}$, $Al_{0.2}Fe_{0.8}$) or (2) for $Cs_2MSi_5O_{12}$ (M=Ni, Mg, Zn, Cd).

Table 1 Refinement data for cubic $CsAlSi_2O_6$ at 298 K Ia-3d (No. 230), a=1.36735 (2) nm

Atom	Site[a]	g[b]	x	y	z	B/nm^2
Cs	16b	1.0	1/8	1/8	1/8	0.033(1)
Al, Si	48g	1.0	0.6628(7)[c]	0.5872(7)	1/8	0.014(2)
O	96h	1.0	0.1020(9)	0.1341(9)	0.7202(9)	0.020(4)

R_{WP}=10.51, R_P=7.28, R_R=10.70, R_e=6.98, S=1.5047, R_I=2.29 and R_F=1.82

[a] Multiplicity and Wykoff notation

[b] Occupancy

[c] Numbers in parentheses are the standard deviations in the last decimal place

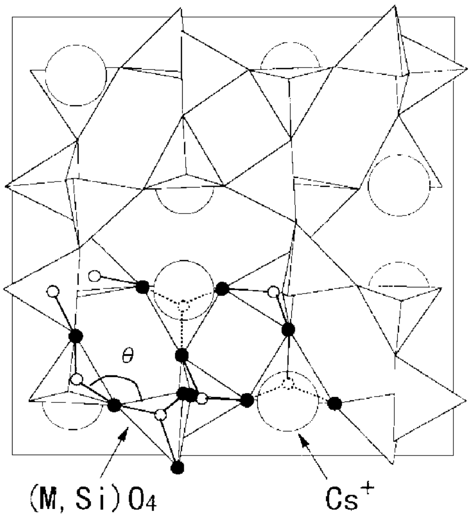

Fig. 8 Crystal structure of the lower half of the unit cell for a cubic leucite-type compound with space group Ia-3d. Open circles and tetrahedra represent Cs^+ ions and (M, Si)O_4 tetrahedra, respectively

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

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

IV means the coordination number. The dashed line (a) in Fig. 9 showed the group for $CsMSi_2O_6$ of which the thermal expansion property had the temperature range of the larger thermal expansion shown in Figs 2 and 3. The dashed line (b) showed the group for $Cs_2MSi_5O_{12}$ and $CsB_{0.2}Al_{0.8}Si_2O_6$ of which the thermal expansion property showed a linear relationship in Figs 2 and 3. Furthermore, for the each dashed line, it was found that the thermal expansions decreased with increasing the bond angle of Si–O–M(Si) for cubic leucite-type compounds at 298 K. In the case of $CsBSi_2O_6$, the value deviated from the dashed line. Where S values in Fig. 9 show the reliability for the result of the Rietveld analysis, the S value for $CsBSi_2O_6$ and $Cs_2ZnSi_5O_{12}$ was not so reliable.

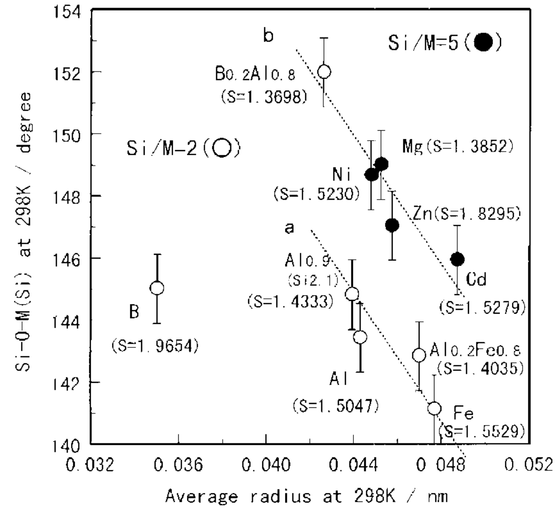

Fig. 9 Relationship between average radius and the bond angle of Si–O–M(Si) at 298 K

Figure 10 shows the relationship between the bond angle of Si–O–M(Si) and the space ratio in the unit cell for cubic leucite-type compounds at 298 K. The space ratio was calculated by the Eq. (3).

$$\text{Space ratio (\%)}=\{1-(\text{Total volume of } {}^{XII}Cs^{+},\ {}^{IV}Si^{4+},\ {}^{IV}O^{2-},\ \text{and } {}^{IV}M^{2+} \text{ or } {}^{IV}M^{3+} \text{ in unit cell})/(\text{Volume of unit cell})\}\times 100 \quad (3)$$

XII and IV mean the coordination number. The dashed lines (c) showed the group for cubic leucite-type compounds which had the linear thermal expansion properties, excluding $Cs_2ZnSi_5O_{12}$ of which the S value seemed not to be reliable. On the other hand, for $CsAlSi_2O_6$ and $Cs_2NiSi_5O_{12}$ the plots were deviated from the dashed lines (c). Considering that the thermal expansion property of $CsAlSi_2O_6$ was similar to

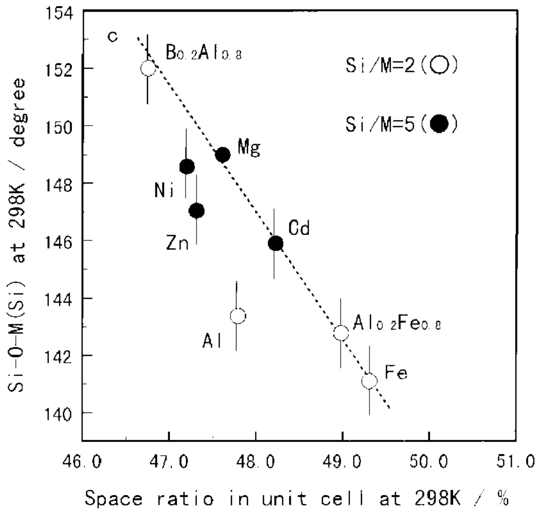

Fig. 10 Relationship between space ratio in unit cell and the bond angle of Si–O–M(Si) at 298 K

that of $Cs_2NiSi_5O_{12}$, it was found that the change of the bond angle of Si-O-M(Si) influenced upon the thermal expansion property of cubic leucite-type compounds. Considering that only $CsAlSi_2O_6$ underwent the phase transition under 298 K, it was found that the phase transition of cubic leucite-type compounds was caused by the difference of the bond angle of Si–O–M(Si) of the framework structure at 298 K.

Conclusions

New cubic leucite-type compounds have been synthesized by the two-stage heat treatment. The thermal expansion properties of the synthesized leucite-type compounds have been studied with HTXRD and LTXRD in the temperature range of 123 to 1273 K. Furthermore, the Rietveld analysis was performed to investigate the factor for phase transitions of the synthesized cubic leucite-type compounds.

The results can be summarized as follows:

(1) The thermal expansion of the synthesized $CsB_{0.2}Al_{0.8}Si_2O_6$ was considerably smaller than that of $CsAlSi_2O_6$. The thermal expansion property of the synthesized $Cs_2MSi_5O_{12}$ (M=Mg, Zn, Cd) showed a linear relationship in the temperature range of 298 to 1273 K and the thermal expansion property of $Cs_2NiSi_5O_{12}$ was similar to $CsAlSi_2O_6$.

(2) The synthesized $CsAlSi_2O_6$ and $Cs_{0.9}Al_{0.9}Si_{2.1}O_6$ underwent the phase transition of tetrahedral to cubic, and the phase transition temperatures were 248 and 173 K, respectively. The linear thermal expansion coefficient of the synthesized $Cs_{0.9}Al_{0.9}Si_{2.1}O_6$ was 2.05×10^{-6}/K in the temperature range of 298 to 1273 K.

(3) The thermal expansion rate decreased with increasing the bond angle of Si–O–M(Si) for cubic leucite-type compounds at 298 K, it was found that the change of the framework structure influenced upon the thermal expansion property, and the phase transition for cubic leucite-type compounds was due to the difference of the bond angle of Si–O–M(Si) of the framework structure in the unit cell at 298 K.

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