Synthesis of Cubic Cs-deficient Pollucite and its Low Thermal Expansion Property
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Pollucite compounds, $\text{Cs}_1-\chi\text{Al}_1-\chi\text{Si}_2-\chi\text{O}_6$ ($\chi=0.0, 0.1, 0.2, 0.25$) with cubic symmetry at 298 K, were synthesized by multi-step heat treatment. The synthesized CsAl$_4$Si$_2$O$_9$ and Cesium$_{12.5}$Al$_{7.5}$Si$_{2.5}$O$_{20}$ were tetragonal below 223 K and 173 K, respectively, while the synthesized $\text{Cs}_6\text{Al}_6\text{Si}_6\text{O}_{24}$ and $\text{Cs}_{12.5}\text{Al}_{7.5}\text{Si}_{2.5}\text{O}_{20}$ were cubic even at 123 K. Cubic Cs$_{7.5}$Al$_{7.5}$Si$_{2.5}$O$_{20}$ showed low thermal expansion in the temperature range of 123 to 1173 K, which is considered that the mean linear thermal expansion coefficient in the range of 123 to 1173 K was $1.47 \times 10^{-6}$ K$^{-1}$. From the relationship between the thermal expansion properties and lattice volumes of the synthesized pollucite compounds, it was concluded that the low thermal expansion properties of Cs$_6\text{Al}_6\text{Si}_6\text{O}_{24}$ and Cs$_{12.5}\text{Al}_{7.5}\text{Si}_{2.5}\text{O}_{20}$ were due to smaller distortion of the aluminosilicate framework compared to Cs$_1-\chi\text{Al}_1-\chi\text{Si}_2-\chi\text{O}_6$ ($\chi=0.0, 0.1$), and that the formation of space around Cs sites in the unit cells resulted in the cubic structure at 123 K for Cs$_1-\chi\text{Al}_1-\chi\text{Si}_2-\chi\text{O}_6$ ($\chi=0.2, 0.25$).

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1. Introduction
Pollucite, CsAl$_4$Si$_2$O$_9$, one of the leucite compounds, is known to have a three dimensional framework structure consisting of 48 (Al, Si)O$_4$ tetrahedra with 16 Cs$^+$ ions occupying large 12-coordinate cavities in the unit cell.$^{1,4}$ Since the crystalline system of pollucite is cubic and (Al, Si)O$_4$ tetrahedra are thermally stable, pollucite has been recognized as a low thermal expansion material in higher temperature ranges.

The thermal expansion property of pollucite shows a large thermal expansion coefficient ($\text{TEC}$; about $12.5 \times 10^{-6}$ K$^{-1}$) in the temperature range of 298 to 473 K and a low TEC (about $2.2 \times 10^{-6}$ K$^{-1}$) in the temperature range of 473 to 1273 K.$^{3,6,7}$ This unique thermal expansion behavior is due to the change of the aluminosilicate framework from a "collapsed form" to an "expanded form" by the rotation of (Si, Al)/O$_4$ tetrahedra with increasing temperature.$^{1,7,4}$ The above knowledge suggested that control of the crystal structure is an important approach for suppression of the large thermal expansion in the range of 298 to 473 K, resulting in low thermal expansion pollucite compounds.

We reported pollucite compounds with various chemical compositions synthesized by the multi-step heating method in order to decrease the amount of Cs$^+$ ions in the crystal structure. The method was more effective for synthesis of the pollucite compounds with cubic, space group Ia-3d, in comparison with hydrothermal methods.$^{1,3}$ As a result, it was found that Cs-deficient pollucite, Cs$_{6}\text{Al}_6\text{Si}_6\text{O}_{24}$, cubic with space group Ia3d, synthesized by the multi-step heat treatment, showed lower thermal expansion than CsAl$_4$Si$_2$O$_9$ in the temperature range of 298 to 1173 K.

In this study, thermal expansion properties for synthesized pollucite compounds with various chemical compositions (Cs$_{1-}\chi\text{Al}_1-\chi\text{Si}_2-\chi\text{O}_6$; $\chi=0.0\ldots0.25$) were examined in the temperature range of 123 to 1173 K by powder HTXRD and LTXRD. From the results, the effect of Cs$^+$ ions on the thermal expansion properties and the crystalline system in the viewpoint of crystal structure was investigated.

2. Experimental procedure
2.1 Powder synthesis of Cs$_{1-}\chi\text{Al}_1-\chi\text{Si}_2-\chi\text{O}_6$ ($\chi=0.0, 0.1, 0.2, 0.25$)
Commercially available CsNO$_3$ (99%, Koujundo Kagaku Co., Ltd.), Al$_2$O$_3$ sol and SiO$_2$ sol (Nissan Kagaku Co., Ltd., Japan) were used as starting materials. Firstly, the powder mixtures of Al$_2$O$_3$ and SiO$_2$ with molar ratio of Al/Si = 1.0/2.0 – 0/2.5 were prepared using Al$_2$O$_3$ sol and SiO$_2$ sol by sol-gel processing$^9$ to obtain homogeneous sol mixtures. The sol mixtures were heated at 873 K for 20 h in air to prepare fine powders of Al$_2$O$_3$ and SiO$_2$. Secondly, CsNO$_3$ powder and the adjusted Al$_2$O$_3$/SiO$_2$ fine powder were mixed to give the following four starting powder compositions with chemical formulas: Cs$_{1-}\chi\text{Al}_1-\chi\text{Si}_2-\chi\text{O}_6$ ($\chi=0.0\ldots0.25$), Al/Si = 1.0/2.0, 0.9/2.1, 0.8/2.2, 0.75/2.25. These CsNO$_3$, Al$_2$O$_3$, and SiO$_2$ powders were ball-milled for 24 h using alumina balls in ethanol solvent. Finally, the mixed powders were heated at 873 K for 20 h and then heated at temperatures of 1073 to 1673 K for 5 to 35 h in air to synthesize single phases of cubic pollucite compounds, Cs$_{1-}\chi\text{Al}_1-\chi\text{Si}_2-\chi\text{O}_6$ ($\chi=0.0\ldots0.25$).

Phase identification for a crystalline phase in the synthesized powders was performed by a powder X-ray diffractometer (XRD; Rigaku Co., Ltd., Ru-De-CuX, $40$ kV, $30$ mA) in the scanning range of $20=20$ to $80^\circ$.

2.2 Thermal expansion properties in the temperature range of 123 to 1173 K
Thermal expansion properties of the synthesized cubic pollucite compounds Cs$_{1-}\chi\text{Al}_1-\chi\text{Si}_2-\chi\text{O}_6$ ($\chi=0.0\ldots0.25$) were investigated by the change of lattice constant in the temperature range of 123 to 1173 K. The thermal expansion properties in the temperature range of 123 to 298 K and 298 to 1173 K were investigated by low temperature X-ray diffraction (LTXRD; MXP18VA, CuK$\alpha_1$, $40$ kV, $200$ mA, MAC Science, Japan) and high temperature X-ray diffraction (HTXRD; MXP18VA, CuK$\alpha_1$, $40$ kV, $200$ mA, MAC Science, Japan), respectively.

In the case of pollucite compounds with cubic symmetry, the lattice constants in the temperature range of 123 to 1173 K were calculated by the least-squares method with six peaks of (332), (440), (611), (631), (721) and (561) planes which were corrected in the scanning range of $20$ to $60^\circ$, using Si as the external standard at the scanning speed of $1^\circ$ min$^{-1}$. In the case of pollucite compounds with tetragonal symmetry, the six or seven peaks of (332), (404), (523), (631), (721), (723) and/or (327) planes were corrected to calculate the lattice
Table 1. Heating Process and Lattice Constant at R.T for Synthesized Cs$_{1-x}$Al$_{1-x}$Si$_2$O$_6$ (X = 0.0, 0.1, 0.2, 0.25)

<table>
<thead>
<tr>
<th>X</th>
<th>Heat treatment</th>
<th>Lattice constant / nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>873K-20h</td>
<td>1.3679(1)</td>
</tr>
<tr>
<td>0.1</td>
<td>1673K-10h</td>
<td>—</td>
</tr>
<tr>
<td>0.2</td>
<td>1673K-10h</td>
<td>1.3668(1)</td>
</tr>
<tr>
<td>0.25</td>
<td>1673K-20h</td>
<td>1.3653(1)</td>
</tr>
</tbody>
</table>

3. Results

3.1 Synthesis of the cubic pollucite compounds

Figure 1 shows that XRD patterns of the obtained samples for Cs$_3$Al$_8$Si$_2$O$_6$ by heating mixed powders at 873 K for 20 h; (a), 873 K for 20 h and 1673 K for 10 h; (b), 873 K for 20 h and 1073 K for 10 h; (c), 873 K for 20 h and 1073 K for 10 h and 1273 K for 35 h; (d).

As the first step in the heat treatment, thermal decomposition of CsNO$_3$ was performed at thermal decomposition temperature, 873 K, determined by TG-DTA measurement. All powder mixtures for Cs$_{1-x}$Al$_{1-x}$Si$_2$O$_6$ (X = 0.0, 0.1, 0.2, 0.25) showed the same thermal decomposition behavior that CsAlSi$_2$O$_6$. XRD patterns for the samples heated at 873 K for 20 h in air showed an amorphous phase, suggesting that CsNO$_3$ was completely decomposed at these conditions. For instance, the amorphous phase for Cs$_3$Al$_8$Si$_2$O$_6$ is shown in Fig. 1(a).

For the second step, heat treatment for Cs$_3$Al$_8$Si$_2$O$_6$ was performed at 1673 K for 10 h, similar to that for Cs$_{1-x}$Al$_{1-x}$Si$_2$O$_6$ (X = 0.0, 0.1). XRD pattern obtained by the heat treatment is shown in Fig. 1(b). Diffraction lines due to the CsAlSi$_2$O$_6$ phase appear in the XRD pattern at around 2θ = 22°, 24°, 27°. The XRD patterns suggest that synthesis of Cs$_3$Al$_8$Si$_2$O$_6$ single phase was more difficult than Cs$_{1-x}$Al$_{1-x}$Si$_2$O$_6$ (X = 0.0, 0.1) due to fewer Cs$^+$ ions for Cs$_3$Al$_8$Si$_2$O$_6$ than Cs$_{1-x}$Al$_{1-x}$Si$_2$O$_6$ (X = 0.0, 0.1).

In order to suppress the production of CsAl$_2$O$_4$, the amorphous powder for Cs$_3$Al$_8$Si$_2$O$_6$ was heated at 1073 K for 10 h in air, as the second step of the treatment, following the first step heat. Subsequently, the Cs$_3$Al$_8$Si$_2$O$_6$ phase and amorphous phase are recognized as shown in Fig. 1(c), Then, the third step of heat treatment for the above mixed phases powder was performed at 1273 K for 35 h in air. The result shows that Cs$_{1-x}$Al$_{1-x}$Si$_2$O$_6$ single phase was synthesized in the XRD pattern as shown in Fig. 1(d). Similarly, Cs$_{0.75}$Al$_{0.25}$Si$_2$O$_6$ single phase was synthesized by the multi-step heat treatment. Table 1 shows the heat treatment conditions for synthesis for the single phases of Cs$_{1-x}$Al$_{1-x}$Si$_2$O$_6$ (X = 0.0, 0.1, 0.2, 0.25) and lattice constants at R.T for the synthesized compounds.

The XRD patterns at R.T for the synthesized compounds, Cs$_{1-x}$Al$_{1-x}$Si$_2$O$_6$ (X = 0.0–0.25), are shown in Fig. 2. Since all of the diffraction lines in the XRD patterns are indexed as pollucite, CsAlSi$_2$O$_6$ (JCPDS card; No. 29-0407), it is found that the synthesized Cs$_{1-x}$Al$_{1-x}$Si$_2$O$_6$ (X = 0.0, 0.1, 0.2, 0.25) had cubic structure with Ia-3d, space group, similar to CsAlSi$_2$O$_6$.

3.2 Thermal expansion properties for the synthesized pollucite compounds

Lattice constants as a function of temperature in the range of 123 to 1173 K together with XRD patterns (2θ = 50–65°) at 123 K for the synthesized pollucite compounds, Cs$_{1-x}$Al$_{1-x}$Si$_2$O$_6$ (X = 0.0–0.25), are shown in Fig. 3(a) to (d).

Figure 3(a) shows that the XRD pattern at 123 K for CsAlSi$_2$O$_6$ and thermal change of lattice constants in the temperature range of 123 to 1173 K. Divergence in the XRD pattern was observed at 123 K, not consistent with the XRD pattern for CsAlSi$_2$O$_6$ at 298 K as shown in Fig. 2. The diverged
Fig. 2. XRD patterns for the synthesized Cs\(_{1-x}\)Al\(_x\)Si\(_2\)O\(_6\), X = 0.0; (a), X = 0.10; (b), X = 0.20; (c), X = 0.25; (d).

Fig. 3. XRD patterns at 123 K and lattice constants in the temperature range of 123 to 1173 K of the synthesized Cs\(_{1-x}\)Al\(_x\)Si\(_2\)O\(_6\) (X = 0.0, 0.1, 0.2, 0.25). ▼ shows diverged diffraction peaks in Figs. 3(a) and (b).

peaks are indicated using ▼ symbols in Fig. 3(a). A similar difference in XRD patterns has been recognized in the case of structural phase transformation of tetragonal to cubic for KAlSi\(_2\)O\(_4\),\(^{19}\) and RbAlSi\(_2\)O\(_4\).\(^{11}\) That is, the divergence for the diffraction lines at 123 K shows that CsAlSi\(_2\)O\(_6\) underwent a structural phase transition from tetragonal to cubic. Since the lattice parameter a for the a-axis increased to around 223 K and lattice parameter c for the c-axis decreased to around 223 K with increasing temperature, CsAlSi\(_2\)O\(_6\) has the structural phase transition of tetragonal to cubic at around 223 K. The lattice constant a for cubic CsAlSi\(_2\)O\(_6\) clearly increased in the temperature range of 223 to 473 K.

Cs\(_{0.9}\)Al\(_{0.1}\)Si\(_2\)O\(_6\) at 123 K shows slight divergence for the diffraction lines in the XRD patterns as shown in Fig. 3(b). Since lattice parameter a increased and lattice parameter c decreased up to 173 K, it was recognized that Cs\(_{0.9}\)Al\(_{0.1}\)Si\(_2\)O\(_6\) underwent a structural phase transition from tetragonal to cubic at around 173 K. In the temperature range of 173 to 373 K,
the lattice constant a for cubic Cs$_{0.8}$Al$_6$Si$_2$O$_8$ clearly increased.

The synthesized CsAlSi$_2$O$_6$ and Cs$_{0.8}$Al$_6$Si$_2$O$_8$ have the same tendency for the structural phase transition as the reported CsAlSi$_2$O$_6$ and Cs$_{0.8}$Al$_6$Si$_2$O$_8$. On the other hand, the synthesized Cs$_{0.75}$Al$_{0.75}$Si$_2$O$_8$ and Cs$_{0.75}$Al$_{0.75}$Si$_2$O$_8$ were cubic at 123 K from the XRD patterns shown in Fig. 3(c) and (d). The lattice constants for both Cs$_{0.8}$Al$_6$Si$_2$O$_8$ and Cs$_{0.75}$Al$_{0.75}$Si$_2$O$_8$ hardly increased in the temperature range of 123 to 1173 K, compared to those for CsAlSi$_2$O$_6$ and Cs$_{0.8}$Al$_6$Si$_2$O$_8$.

Here, Td was used as end point of temperature$^1$ in the region for “rapid thermal expansion” due to the structural change of “a collapsed form at R.T$^1$ to “an expanded form”.

Figure 4 shows the thermal expansion properties of the synthesized Cs$_{1-x}$Al$_{1-x}$Si$_2$O$_8$ (X = 0.0, 0.1) in the temperature range of 298 to 1173 K. CsAlSi$_2$O$_6$ and Cs$_{0.8}$Al$_6$Si$_2$O$_8$, which underwent the structural phase transition of tetragonal to cubic, showed the lowest thermal expansion properties in the temperature range of 298 to 473 K and 298 to 373 K, respectively. Whereas, Cs$_{0.75}$Al$_{0.75}$Si$_2$O$_8$ and Cs$_{0.75}$Al$_{0.75}$Si$_2$O$_8$, cubic even at 123 K, showed the lowest thermal expansion properties in the temperature range of 298 to 1173 K, without the large thermal expansion showed in thermal expansion properties for CsAlSi$_2$O$_6$ and Cs$_{0.8}$Al$_6$Si$_2$O$_8$. In particular, Cs$_{0.75}$Al$_{0.75}$Si$_2$O$_8$, had a mean linear thermal expansion coefficient of 1.47 $\times$ $10^{-6}$ K$^{-1}$ in the temperature range of 123 to 1173 K.

4. Discussion

4.1 Effect of alkaline metal ionic radius on lattice constant at Td

The relationship between the lattice constant at Td as shown in Fig. 4 and average ionic radius of alkaline metal ions for the synthesized Cs$_{1-x}$Al$_{1-x}$Si$_2$O$_8$ (X = 0.0, 0.1, 0.2, 0.25) in the temperature range of 298 to 1173 K, Td$^1$, was investigated. The result is shown in Fig. 5. The average ionic radii of Cs$^+$ ions, R$_{CS}^{AVE}$, were calculated based on equation (1).

$$R_{CS}^{AVE} = 0.188 \times (1 - X)$$

Similarly, the ionic radii for Rb$^+$ ion in RbAlSi$_2$O$_6$ and K$^+$ ion in KAlSi$_2$O$_6$ were 0.172 nm and 0.164 nm, respectively, referring to shannon’s values.$^{15}$

As shown in Fig. 5, the lattice constant at Td for both MAI$_2$O$_6$ (M = Cs, Rb, K) and Cs$_{1-x}$Al$_{1-x}$Si$_2$O$_8$ (X = 0.0 $\sim$ 0.25) systems monotonously decreases with decreasing ionic radius of alkaline metal ions. Thus, the changing rate of lattice constant as a function of R$_{AVE}$ for the synthesized Cs$_{1-x}$Al$_{1-x}$Si$_2$O$_8$ (X = 0.0 $\sim$ 0.25) system is smaller than that for the MAI$_2$O$_6$ (M = Cs, Rb, K) system.

As for the decrease in alkaline metal ion radius, in the case of MAI$_2$O$_6$ (M = Rb, K), space increases around each of the W sites in the unit cell, due to the ionic radii for K$^+$ and Rb$^+$ ions smaller than Cs$^+$ ions. Whereas, in the case of the Cs$_{1-x}$Al$_{1-x}$Si$_2$O$_8$ (X = 0.0 $\sim$ 0.25) system, a decrease in the amount of Cs$^+$ ions resulted in the formation of partial space in Cs sites, W sites, in the unit cell. From the above viewpoint, it is considered that the formation of partial space in Cs sites decreased the change of lattice constant with a decrease in R$_{AVE}$ for the Cs$_{1-x}$Al$_{1-x}$Si$_2$O$_8$ (X = 0.0 $\sim$ 0.25) system. Therefore, aluminosilicate framework structures easily have the cubic structure at R.T in the case of the existence of Cs$^+$ ions in 12-coordinated sites of the unit cells.

4.2 Effect of Cs$^+$ ions amount on the rapid thermal expansion

To investigate the effect of Cs$^+$ ions on the thermal expansion properties, the relationship between Cs$^+$ ions and lattice volume at R.T, $V_{RT}$ ( ), is shown in Fig. 6. The $V_{RT}$ increased with increasing amount of Cs$^+$ ions, while the rate of increase for $V_{RT}$ in the range of 0.9 to 1.0 decreased. In the case above 0.9 of Cs$^+$ ions, an increase in lattice constant was suppressed and resulted in the formation of a “distorted three-dimensional framework”.

In order to investigate the relationship between the distortion and thermal expansion, the difference, $\Delta V$, between the Cs$^+$ ions volumes for Cs$_{1-x}$Al$_{1-x}$Si$_2$O$_8$ (X = 0.0, 0.1, 0.2)
and those for Cs$_{0.75}$Al$_{0.25}$Si$_2$O$_6$ were calculated according to equation (2). Here, 0.188 nm is the ionic radius$^{30}$ of Cs$^+$ ion for 12-coordinated sites.

\[
\Delta V_c = (X - 0.75) \times 4/3\pi \times 0.188^3 \text{ (nm}^3) \tag{2}
\]

Values, $V_{RT}$ (•), calculated by adding $V_{RT}$ to $\Delta V_c$, at each amount of Cs$^+$ ions, are also plotted in Fig. 6. The $V_{RTC}$ increased linearly with increasing amount of Cs$^+$ ions, and $\Delta V_c$ is consistent with amount of decrease for lattice volume due to the distortion at R.T in the structural frameworks for Cs$_{1-X}$Al$_{1-X}$Si$_{2}$O$_6$ (X = 0.0, 0.1) from the curve for $V_{RT}$ (•). Furthermore, volumes $V_{RT}$ at Td in Fig. 4 for Cs$_{1-X}$Al$_{1-X}$Si$_{2}$O$_6$ (X = 0.1), shown as plots (△) in Fig. 6, are almost consistent with $V_{RTC}$ for Cs$_{1-X}$Al$_{1-X}$Si$_{2}$O$_6$ (X = 0.0, 0.1). That is, it was clarified that $V_{RTC}$ meant lattice volume for the forming of a “non-distorted structure” at R.T in the pollucite structure.

4.3 Effect of lattice volume below R.T on crystalline symmetry

Lattice volumes for Cs$_{1-X}$Al$_{1-X}$Si$_{2}$O$_6$ (X = 0.0–0.25) as a function of temperature in the range of 123 to 373 K are shown in Fig. 7. The lattice volumes for Cs$_{0.75}$Al$_{0.25}$Si$_2$O$_6$ and Cs$_{0.75}$Al$_{0.25}$Si$_2$O$_6$ monotonously increased with increasing temperature, while CsAlSi$_2$O$_6$ and CsAl$_6$Si$_3$O$_8$ have similar behaviors for lattice volumes in the temperature range of 123 to 223 K, in which the crystalline symmetry of CsAlSi$_2$O$_6$ and CsAl$_6$Si$_3$O$_8$ are tetragonal. Above 223 K, the lattice volumes of their compounds rapidly expanded up to 298 K. Thus, changing rates for lattice volumes in the temperature range of 123 to 373 K are found to decrease with decreasing amount of Cs$^+$ ions.

On the other hand, all of the lattice volumes of Cs$_{1-X}$Al$_{1-X}$Si$_{2}$O$_6$ (X = 0.0–0.25) at 123 K existed in region of ca.2.533 to ca.2.538 nm$^3$. Since Cs$_{1-X}$Al$_{1-X}$Si$_{2}$O$_6$ (X = 0.2, 0.25) are cubic, and Cs$_{1-X}$Al$_{1-X}$Si$_{2}$O$_6$ (X = 0.0, 0.1) are tetragonal at 123 K, regardless of their crystalline symmetry, Cs$_{1-X}$Al$_{1-X}$Si$_{2}$O$_6$ (X = 0.0–0.25) are found to have similar lattice volumes at 123 K. The result shows that Cs$_{0.75}$Al$_{0.25}$Si$_2$O$_6$ and Cs$_{0.75}$Al$_{0.25}$Si$_2$O$_6$ were able to be cubic at 123 K, due to the amount of Cs$^+$ ions, smaller than Cs$_{1-X}$Al$_{1-X}$Si$_{2}$O$_6$ (X = 0.0, 0.1). That is, it was considered that the amount of Cs$^+$ ions in the unit cell classified Cs$_{1-X}$Al$_{1-X}$Si$_{2}$O$_6$ (X = 0.0–0.25) into cubic and tetragonal structure at 123 K.

5. Conclusions

Thermal expansion properties in the temperature range of 123 to 1173 K for the synthesized pollucite compounds were investigated by LTXRD and HTXRD. The obtained results were as follows:

1) Cubic pollucite compounds, Cs$_{1-X}$Al$_{1-X}$Si$_{2}$O$_6$ (X = 0.0, 0.1, 0.2, 0.25), were synthesized by the multi-step heat treatment.

2) The synthesized Cs$_{1-X}$Al$_{1-X}$Si$_{2}$O$_6$ (X = 0.2, 0.25), cubic in the temperature range of 123 to 1173 K, without the structural phase transition undergoing in CsAlSi$_2$O$_6$ and Cs$_{0.75}$Al$_{0.25}$Si$_2$O$_6$, showed low thermal expansion properties in the range of 123 to 1173 K.

3) The amount of Cs$^+$ ions in the unit cell was concerned with the rapid thermal expansions above R.T and the crystalline symmetry below R.T for Cs$_{1-X}$Al$_{1-X}$Si$_{2}$O$_6$ (X = 0.0, 0.1, 0.2, 0.25).

References
