

# Thermal Expansion Characteristics of Li-Replaced Type Pollucite ( $\text{Cs}_{1-x}\text{Li}_x\text{AlSi}_2\text{O}_6$ ) Powder

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## Li 置換型ポルーサイト ( $\text{Cs}_{1-x}\text{Li}_x\text{AlSi}_2\text{O}_6$ ) 粉末の熱膨張特性

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**Pollucite ( $\text{Cs}_{1-x}\text{Li}_x\text{AlSi}_2\text{O}_6$ ) powders of single phase have been synthesized by isomorphous replacement of part of the  $\text{Cs}^+$  ion by  $\text{Li}^+$  ion in the pollucite structure using sol-gel processing. Thermal expansion of the synthesized powder has also been investigated with a high-temperature XRD. The pollucite powders of single phase were synthesized in the case of the composition ( $\text{Cs}_2\text{O} : \text{Li}_2\text{O} : \text{SiO}_2 : \text{Al}_2\text{O}_3$  (molar ratio) = 0.95-0.90 : 0.05-0.10 : 4.5 : 1). Thermal expansion was less than 0.2% (room temperature to 1200°C). In particular, the powders showed almost zero thermal expansion in the range of room temperature to 500°C.**

**Key-words:** Pollucite, Sol-gel, Thermal expansion, Li, Isomorphous replacement

### 1. Introduction

Pollucite ( $\text{CsAlSi}_2\text{O}_6$ ) has been known as a low thermal expansion ceramics, but literature<sup>1)-2)</sup> for its thermal expansion behavior is rather limited. The authors have prepared pollucite powders of single phase by sol-gel processing and examined thermal expansion behavior. An apt selection of pollucite composition and the heat treatment conditions were eventually effective in lowering the thermal expansion of the pollucite powders.<sup>3)-4)</sup> For the powder of excess  $\text{SiO}_2$  (molar ratio of  $\text{Cs}_2\text{O} : \text{SiO}_2 : \text{Al}_2\text{O}_3 = 1 : 4.5-5 : 1$ ), the thermal expansion of the pollucite was particularly lowered in the range of room temperature to 200°C.<sup>4)</sup> It is thought that this effect results in the transition to the 4-ring "spread structure"<sup>1),5)</sup> which contains no  $\text{Cs}^+$  ion configuration in the pollucite structure.

In this study, we prepared Li-replaced type pollucite powders, which replaced a part of  $\text{Cs}^+$  ion in a pollucite structure by  $\text{Li}^+$  ion isomorphously. The substitution of the  $\text{Cs}^+$  and  $\text{Li}^+$  ions is assumed to be very fast and proceeds almost quantitatively.<sup>2)</sup> This should be feasible to synthesize pollucite powders with a lower thermal expansion. In the alumino sili-

cate system, a few examples<sup>2),6)-9)</sup> have been reported upon the lowering of thermal expansion by replacing part of the constituent atom by another atom or by adding another atom.

### 2. Experimental procedure

$\text{Al}_2\text{O}_3$  sol and  $\text{SiO}_2$  sol were adjusted to pH 5.5 with the addition of aqueous ammonia respectively, and then mixed. The mixture (molar ratio of  $\text{SiO}_2/\text{Al}_2\text{O}_3 = 4.5/1$  or  $5/1$ ) was evaporated to remove water, after being stirred for 20 h. Trace amounts of water were then removed with ethanol, and the powder mixture was heated at 550°C for 2 h. Powder samples were prepared by adding  $\text{CsNO}_3$  and  $\text{LiNO}_3$  at specified molar ratios ( $\text{Cs}_2\text{O} : \text{Li}_2\text{O} : \text{SiO}_2 : \text{Al}_2\text{O}_3 = 0.95-0.80 : 0.05-0.20 : 4.5 : 1$ , hereinafter called Sample Cs-0.95, Sample Cs-0.90 and Sample Cs-0.80), wet mixing them together with ethanol and alumina balls in plastic pots for 24 h and drying them. The powdered samples were calcined at 1000°C for 50 h, after being heated at 600°C for 24 h and at 750°C for 10 h (so-called two-stage heat treatment).

The identification of a crystal phase and the measurement of lattice constants of the pollucite were performed by means of a powder X-ray diffractometer (Cu  $K\alpha$  ray, 40 kV, 30 mA). The lattice constants were calculated from  $2\theta$  by the least-squares method (utilizing application software made in Rigaku Denki), after the six peaks of (332), (431), (440), (611), (444) and (721) appearing at  $2\theta$  of 25°-55° were corrected using Si as the external standard. The thermal expansion of the pollucite powders of single phase was also calculated from the lattice constants at various temperatures with a high-temperature X-ray diffractometer; the same procedure as described above was followed to obtain the lattice constants. The measurements obtained were a scanning range of  $2\theta$  of 25°-55°, scanning speed of 10 k/min, and step in temperature of every 50°C at room temperature-400°C and every 100°C at 400°-1200°C.

### 3. Results and discussion

#### 3.1 Synthesis of pollucite powder by isomorphous replacement of a part of Cs by Li

The XRD patterns of the products (Sample Cs-0.95, Sample Cs-0.90 and Sample Cs-0.80 above calcined at 1000°C for 50 h after heated at 600°C for 24 h and at 750°C for 10 h (two-stage heat treatment)) are shown in Fig. 1. It was found that pollucite powders ( $\text{Cs}_{1-x}\text{Li}_x\text{AlSi}_2\text{O}_6$ ) of single phase by isomorphous replacement of part of the  $\text{Cs}^+$  ion by  $\text{Li}^+$  ion were synthesized from Sample Cs-0.95 and Sample Cs-0.90. On the other hand, the pollucite phase and  $\beta$ -spodumene phase were identified concurrently in the products of Sample Cs-0.80. These phases have not changed for a recalced powder at 1200°C for 2 h. When the sample powders, of which the molar ratio of  $\text{SiO}_2$  increased from 4.5 to 5, were treated under the conditions described above, a trace amount of  $\text{CsAlSi}_5\text{O}_{12}$  phase was identified in all of them.

The lattice constants of  $\text{Cs}_{1-x}\text{Li}_x\text{AlSi}_2\text{O}_6$  of single phase at room temperature were  $a = 13.657 \pm 0.003 \text{ \AA}$  and  $a = 13.655 \pm 0.003 \text{ \AA}$  in Cs-0.95 and Cs-0.90, respectively, and these values agreed with that of Li free ( $a = 13.651 \pm 0.004 \text{ \AA}$ ) in the cases of Sample Cs-0.95 and Sample Cs-0.90.

#### 3.2 Thermal expansion behavior of the $\text{Cs}_{1-x}\text{Li}_x\text{AlSi}_2\text{O}_6$ powder of single phase

The relationship between thermal expansion and the temperature of synthesis of the  $\text{Cs}_{1-x}\text{Li}_x\text{AlSi}_2\text{O}_6$  powder from Sample Cs-0.95 and Sample Cs-0.90 is shown in Fig. 2. The result with Sample Cs-1.0<sup>4)</sup> ( $\text{Cs}_2\text{O} : \text{SiO}_2 : \text{Al}_2\text{O}_3 = 1 : 4.5 : 1$ ) is also shown for comparison. Similar trends were observed for Sample Cs-0.95 and Sample Cs-0.90, although the curves as a whole were shifted down to lower thermal expansion in the range of room temperature to 1200°C. These samples showed almost zero thermal expansion

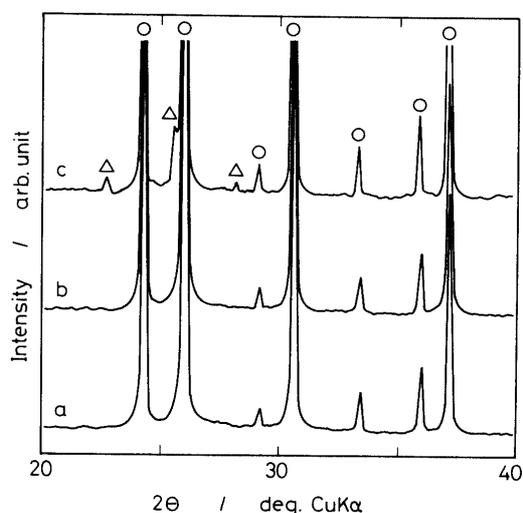


Fig. 1. X-ray powder diffraction patterns of the products calcined at 1000°C for 50 h after heating at 600°C for 24 h and at 750°C for 10 h.

a : Sample Cs-0.95, b : Sample Cs-0.90, c : Sample Cs-0.80  
○ :  $\text{CsAlSi}_2\text{O}_6$ , △ :  $\text{LiAlSi}_2\text{O}_6$

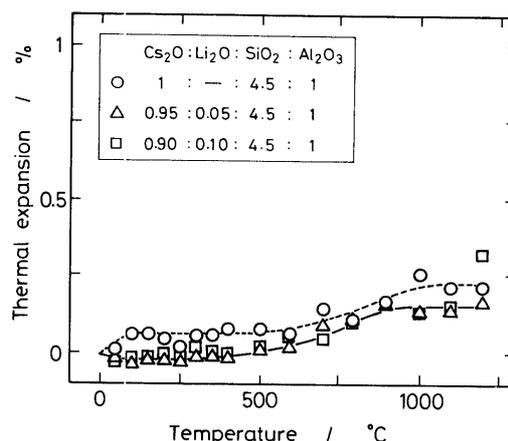


Fig. 2. Relation between temperature and thermal expansion of the pollucite powder obtained using various  $\text{Cs}_2\text{O} : \text{Li}_2\text{O}$  (molar ratio) compositions. Heat treatment condition : 600°C for 24 h, 750°C for 10 h and 1000°C for 50 h.

for the range from room temperature to 500°C, and the thermal expansion maintained was less than 0.2% up to 1200°C. Thus, the isomorphous replacement of part of the  $\text{Cs}^+$  ion in the pollucite structure by  $\text{Li}^+$  ion decreased the thermal expansion.

From these results, the difference in ionic radius of the alkaline metals replaced varies the proportion of "open space" ( $\text{Li}^+$  ion occupancy of the cavity of 4-ring is possible<sup>8)</sup>) in a continuous polyhedron made up of aluminosilicates in the pollucite structure. Exact control is possible in the range (lattice parameters do not change) of which a residual  $\text{Cs}^+$  ion can maintain the pollucite structure. It can therefore be that a proportion of "open space" affects a relaxation of heat motion in the lattice, and as a result the thermal expansion decreases when heat motion in the lattice is relaxed depending upon the isomorphous replacement of part of the  $\text{Cs}^+$  ion by  $\text{Li}^+$  ion.

### 4. Conclusion

The pollucite powders by the isomorphous replacement of part of the  $\text{Cs}^+$  ion in the pollucite structure by  $\text{Li}^+$  ion were synthesized to produce lower thermal expansion. The influence of the isomorphous replacement on the thermal expansion behavior was studied. This resulted in the following:

(1) In  $\text{SiO}_2$  molar ratio = 4.5, the  $\text{Cs}_{1-x}\text{Li}_x\text{AlSi}_2\text{O}_6$  powder of single phase was synthesized in the case of the composition ( $\text{Cs}_2\text{O} : \text{Li}_2\text{O} : \text{SiO}_2 : \text{Al}_2\text{O}_3 = 0.95-0.90 : 0.05-0.10 : 4.5 : 1$ ). On the other hand, the  $\text{CsAlSi}_5\text{O}_{12}$  phase and  $\beta$ -spodumene phase were formed in  $\text{SiO}_2$  molar ratio = 5 and  $\text{Li}_2\text{O}$  molar ratio = 0.20 ( $\text{Cs}_2\text{O} = 0.80$ ) respectively.

(2) The thermal expansion rate of the synthesized pollucite powders of single phase maintained in an increase within 0.2% in the range of room temperature to 1200°C. In particular, these powders had almost zero thermal expansion in the range of room temperature to 500°C.

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