

# Sintering of Pollucite Using Amorphous Powder and Its Low Thermal Expansion Property

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## 非晶質仮焼粉末を用いたポルルサイトの焼結とその低熱膨張特性

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Calcined powders were prepared for sintering of cubic  $\text{Cs}_{0.9}\text{Al}_{0.9}\text{Si}_{2.1}\text{O}_6$  by calcining a mixture of  $\text{Al}_2\text{O}_3/\text{SiO}_2$  fine powder and  $\text{CsNO}_3$  powder at temperatures of 798 to 1123 K for 20 h in air. The amorphous phase produced in the case of a lower calcination temperature, while the crystallinity of the calcined powder increased with increasing calcination temperature. Densification of the  $\text{Cs}_{0.9}\text{Al}_{0.9}\text{Si}_{2.1}\text{O}_6$  green body was significantly enhanced using the amorphous calcined powder. The relative density of the  $\text{Cs}_{0.9}\text{Al}_{0.9}\text{Si}_{2.1}\text{O}_6$  sintered body reached 94.5% when the green body of the amorphous calcined powder, including a slight amount of  $\text{CsNO}_3$ , was sintered at 1673 K for 20 h in air. The dense cubic  $\text{Cs}_{0.9}\text{Al}_{0.9}\text{Si}_{2.1}\text{O}_6$  sintered body showed linear thermal expansion without hysteresis, resulting in a thermal expansion rate of ca. 0.13% at 1273 K.

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### 1. Introduction

Pollucite,  $\text{CsAlSi}_2\text{O}_6$ , is a cubic zeolite-related compound which consists of 16  $\text{Cs}^+$  ions and a three-dimensional aluminosilicate framework of 48 (Si, Al) $\text{O}_4$  tetrahedra in a unit cell,<sup>1,2)</sup> and can be used up to high temperatures because of its high melting point, that is, >2173 K.<sup>3)</sup> Pollucite exhibits a unique thermal expansion curve that has two stages: In the first stage, large thermal expansion in the low-temperature range of RT (298 K) to 473 K. Here, the average linear thermal expansion coefficient (hereafter TEC) was ca.  $1.0 \times 10^{-5}/\text{K}$ .<sup>1,4)-7)</sup> In the second stage, small thermal expansion in the range of 473 to 1273 K (TEC: ca.  $2.0 \times 10^{-6}/\text{K}$ ).<sup>1,4)-7)</sup> Therefore, pollucite is expected to be a new cubic low thermal expansion material by lowering the thermal expansion rate in the low-temperature range.

Recently, we have found that cubic Cs-deficient pollucite,  $\text{Cs}_{0.9}\text{Al}_{0.9}\text{Si}_{2.1}\text{O}_6$ , showed a lower thermal expansion property in its temperature range of 298 to 1273 K<sup>8)-10)</sup> without the large thermal expansion observed in pollucite. On the other hand, as for sintering of pollucite, it was reported that pollucite glass ceramics<sup>11),12)</sup> and pollucite sintered bodies<sup>13)</sup> including glass phases, with a 91% relative density, were obtained by hot pressing at 1913 K. However, there is no report on fabrication of dense pollucite sintered under atmospheric pressure.

In this paper, densification of a  $\text{Cs}_{0.9}\text{Al}_{0.9}\text{Si}_{2.1}\text{O}_6$  sintered body with a low thermal expansion property was attempted under atmospheric pressure via reaction sintering using calcined powders for the green body. The thermal expansion behavior of the obtained dense  $\text{Cs}_{0.9}\text{Al}_{0.9}\text{Si}_{2.1}\text{O}_6$  sintered body was investigated in the temperature range of 298 to 1273 K.

### 2. Experimental procedure

Commercially available  $\text{Al}_2\text{O}_3$  sol (Aluminum Sol 200, Nissan Chemical Ind., Ltd.),  $\text{SiO}_2$  sol (Snotex O, Nissan Chemical Ind., Ltd.), and  $\text{CsNO}_3$  powder (99% up, Kojundo Chemical Lab. Co., Ltd.) were used as starting raw materials. The  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  sols were adjusted to pHs 5.3-5.5 with ammonia water. Then these sols were mixed at an Al :

Si molar ratio of 0.9 : 2.1 and stirred for 24 h, followed by treatment in a rotary evaporator to remove water in the sol mixture. A mixed gel was then obtained. The mixed gel was calcined in alumina crucibles at 873 K for 20 h in air. Then the prepared  $\text{Al}_2\text{O}_3/\text{SiO}_2$  fine powder and the  $\text{CsNO}_3$  powder were mixed with the calcined gel to obtain a Cs : Al : Si molar ratio of 0.9 : 0.9 : 2.1 by ball milling in ethanol for 24 h, dried, and subsequently calcined at a designated temperature in the range of 798 to 1273 K for 20 h in air. The calcined powders were shaped into  $5 \times 5 \times 10$  mm compact by uniaxial pressing at 49 MPa and then by cold isostatic pressing (CIP) at 196 MPa. The green bodies obtained were sintered at 1673 K for 20 h in air at a rate of 20 K/min.

The phases present were determined by X-ray diffraction (XRD; Rad-B, Rigaku Co., Ltd., 40 kV, 30 mA) with  $\text{Cu K}\alpha$  radiation within the  $2\theta$  range of 20 to 60°. The specific surface area of the calcined powder was measured from the adsorption isotherm of nitrogen at 77 K by the Brunauer-Emmett-Teller method (BET; Sorptmatic 1990, CE Instruments Corp.). The bulk density of the  $\text{Cs}_{0.9}\text{Al}_{0.9}\text{Si}_{2.1}\text{O}_6$  sintered body was measured using Archimedes' method with deionized water as immersion medium. Relative density was calculated by comparing the bulk density of the sintered body with the theoretical density of  $\text{Cs}_{0.9}\text{Al}_{0.9}\text{Si}_{2.1}\text{O}_6$  that was previously calculated based on the lattice constant ( $= 1.3679 \text{ nm}^3$ ) of the synthesized  $\text{Cs}_{0.9}\text{Al}_{0.9}\text{Si}_{2.1}\text{O}_6$  powder. The microstructure of the fractured surface of the  $\text{Cs}_{0.9}\text{Al}_{0.9}\text{Si}_{2.1}\text{O}_6$  sintered body was observed by scanning electron microscopy (SEM; S-4100, Hitachi Co., Ltd.). Chemical composition was investigated by X-ray fluorescence spectroscopy (XRF; PW2400, Philips Japan, Tokyo). The thermal expansion behavior of the  $\text{Cs}_{0.9}\text{Al}_{0.9}\text{Si}_{2.1}\text{O}_6$  sintered body in the temperature range of 298 to 1273 K was investigated by thermomechanical analysis (TMA; Thermoflex, Rigaku Co., Ltd.) at a rate of 2 K/min for both heating and a cooling.

### 3. Results and discussion

Figures 1(a)-(d) show the XRD patterns of the powders calcined at 798, 873, 1023, and 1123 K for 20 h, respective-

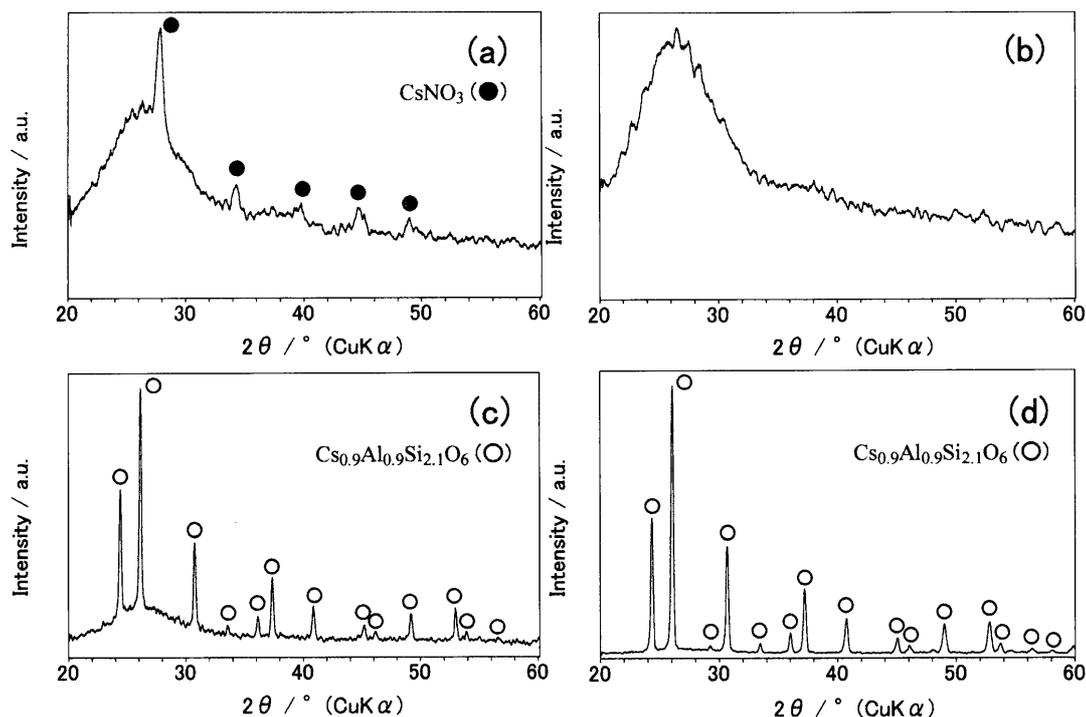


Fig. 1. XRD patterns for the calcined powders obtained by heating the powder mixtures at 798 K (a), 873 K (b), 1023 K (c) and 1123 K (d) for 20 h in air.

ly. In the 798 K-calcined powder, diffraction peaks for  $\text{CsNO}_3$  were observed in addition to the amorphous phase (Fig. 1(a)), while only the amorphous phase was observed (Fig. 1(b)) in the 873 K-calcined powder. On the other hand, the  $\text{Cs}_{0.9}\text{Al}_{0.9}\text{Si}_{2.1}\text{O}_6$  phase was observed in addition to the amorphous phase in the 1023 K-calcined powder (Fig. 1(c)). The crystallinity of the  $\text{Cs}_{0.9}\text{Al}_{0.9}\text{Si}_{2.1}\text{O}_6$  phase increased with increasing calcination temperature. In the case of the powder calcined at 1123 K for 20 h, diffraction peaks for the well-crystallized  $\text{Cs}_{0.9}\text{Al}_{0.9}\text{Si}_{2.1}\text{O}_6$  phase without the amorphous phase were observed (Fig. 1(d)). These calcined powders were classified into four types based on their phases: A) amorphous and  $\text{CsNO}_3$  phases, B) amorphous phase, C) amorphous and crystalline  $\text{Cs}_{0.9}\text{Al}_{0.9}\text{Si}_{2.1}\text{O}_6$  phases, D) crystalline  $\text{Cs}_{0.9}\text{Al}_{0.9}\text{Si}_{2.1}\text{O}_6$  phase.

The specific surface areas of the powders calcined at B) 873 K, C) 1023 K, and D) 1123 K for 20 h were  $12.3 \text{ m}^2/\text{g}$ ,  $7.3 \text{ m}^2/\text{g}$ , and  $4.7 \text{ m}^2/\text{g}$ , respectively. As expected, the specific surface area of the calcined powder decreased as the calcination temperature increased. Here, the specific surface area of powder consists of  $\text{CsNO}_3$  and amorphous phases, was not measured because it contained a small amount of  $\text{CsNO}_3$ .

The sinterability of powders A)–D) was investigated. We have two reasons for our choice of calcination temperatures: the first reason is that higher calcination temperatures cause considerable growth and hard agglomeration of powder particles, which will decrease the sinterability of the powders (particularly powder D)); the second reason is that the amorphous powders obtained by calcination at low temperature enhances the densification of the powders in sintering (particularly powders A and B). Figure 2 shows the relative density of  $\text{Cs}_{0.9}\text{Al}_{0.9}\text{Si}_{2.1}\text{O}_6$  as a function of calcination temperature. The relative density increased up to 94.5% with decreasing calcination temperature from 1123 to 798 K. This result indicates that densification of  $\text{Cs}_{0.9}\text{Al}_{0.9}\text{Si}_{2.1}\text{O}_6$  sintered bodies is enhanced as the specific surface area in-

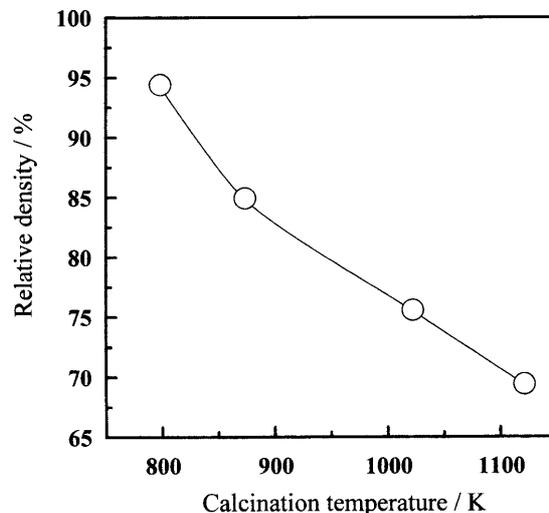


Fig. 2. Relationship between calcination temperature for the mixed raw powders and the relative density of the  $\text{Cs}_{0.9}\text{Al}_{0.9}\text{Si}_{2.1}\text{O}_6$  sintered bodies obtained by heating the green bodies of the calcined powders at 1673 K for 5 h in air.

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Figure 3 shows the microstructures of the fractured surfaces of the  $\text{Cs}_{0.9}\text{Al}_{0.9}\text{Si}_{2.1}\text{O}_6$  specimens sintered using 1123 K-, 1023 K-, and 798 K-calcined powders. In the case of the use of 1123 K-calcined powders, a porous morphology was observed in the fractured surface (Fig. 3(a)), which is due to sintering among particles ca.  $1 \mu\text{m}$  in diameter. The morphology of the sintered body was similar to that of the porous body fabricated in our previous work.<sup>14),15)</sup> When the 1023 K-calcined powder was used, larger pores of various shapes and sizes than those in the case of the 1123 K-

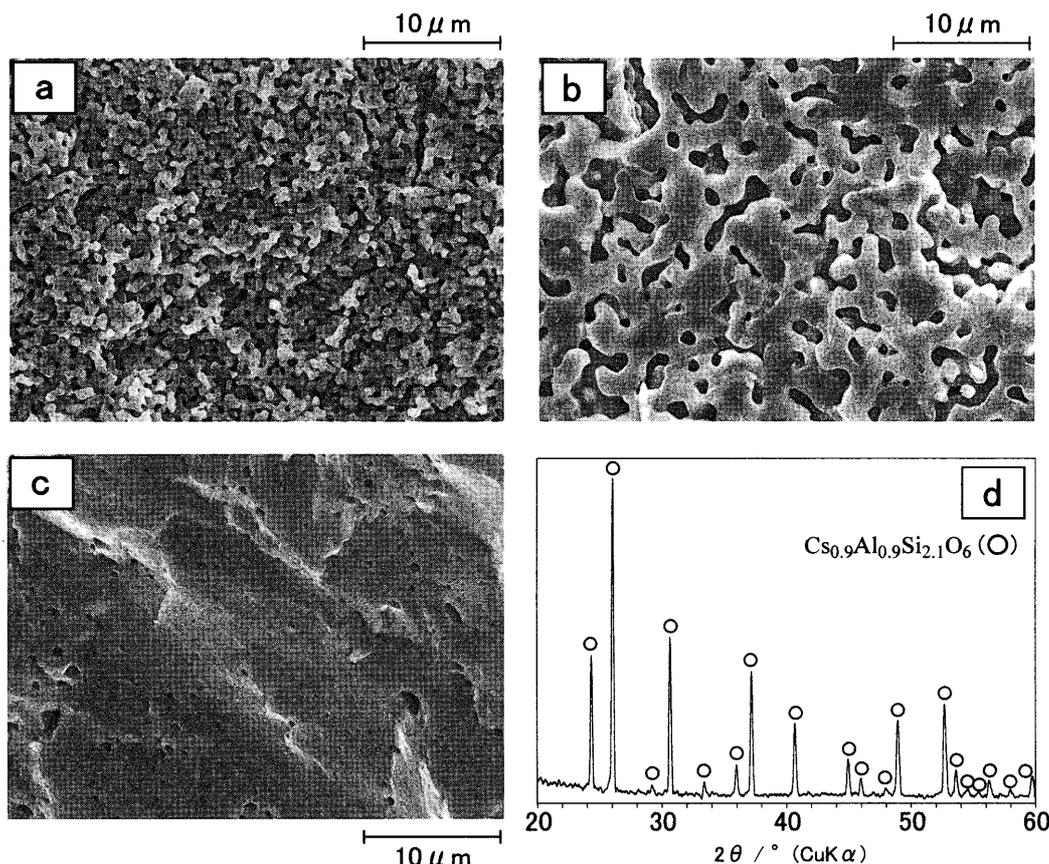


Fig. 3. SEM photographs for the fractured surface of the  $\text{Cs}_{0.9}\text{Al}_{0.9}\text{Si}_{2.1}\text{O}_6$  sintered body fabricated by heating the green body using (a) 1123 K-, (b) 1023 K-, and (c) 798 K-calcined powders at 1673 K for 20 h in air and XRD pattern (d) for the fracture surface (c) of the sintered body.

calcined powder were observed, as shown in Fig. 3(b). The relative density of the sintered body and grain size increased in comparison with the case of the 1123 K-calcined powder. However, a dense  $\text{Cs}_{0.9}\text{Al}_{0.9}\text{Si}_{2.1}\text{O}_6$  sintered body was not fabricated. On the other hand, it was found that a dense  $\text{Cs}_{0.9}\text{Al}_{0.9}\text{Si}_{2.1}\text{O}_6$  sintered body with a relative density of 94.5% was fabricated in the case of the 798 K-calcined powder, although several small pores were observed in the fractured surface shown in Fig. 3(c). Additionally, the sintered body was found to consist of the well-crystallized  $\text{Cs}_{0.9}\text{Al}_{0.9}\text{Si}_{2.1}\text{O}_6$  single phase from the XRD pattern shown in Fig. 3(d).

Thus, a dense  $\text{Cs}_{0.9}\text{Al}_{0.9}\text{Si}_{2.1}\text{O}_6$  sintered body, which had the well-crystallized  $\text{Cs}_{0.9}\text{Al}_{0.9}\text{Si}_{2.1}\text{O}_6$  single phase without a glass phase in the sintered body, was fabricated at a lower temperature than those in previous reports,<sup>11,12)</sup> because the 798 K-calcined powder had the high reactive amorphous phase. This result is to be used as a basis of pressureless sintering of pollucite. Chemical composition of the  $\text{Cs}_{0.9}\text{Al}_{0.9}\text{Si}_{2.1}\text{O}_6$  sintered body investigated by XRF was 0.86/2.10 for Cs/Si in molar ratio. Since the molar ratio of Cs/Si is 0.9/2.1 in  $\text{Cs}_{0.9}\text{Al}_{0.9}\text{Si}_{2.1}\text{O}_6$ , it was clarified that there was insignificant Cs loss during the sintering process.

Figure 4 shows the thermal expansion behavior of the dense cubic  $\text{Cs}_{0.9}\text{Al}_{0.9}\text{Si}_{2.1}\text{O}_6$  sintered body measured using the TMA unit. The dense sintered body was found to exhibit linear and low thermal expansion property with little hysteresis, resulting in a thermal expansion rate of ca. 0.13% at 1273 K (TEC:  $1.3 \times 10^{-6}/\text{K}$  (298–1273 K)). In addition, a parabolic curve for the thermal expansion behav-

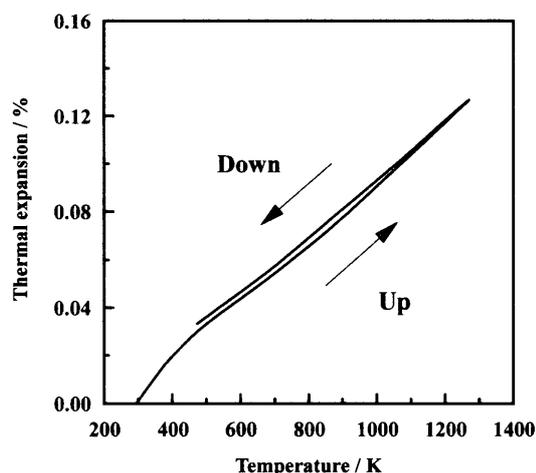


Fig. 4. Thermal expansion behavior of the dense cubic  $\text{Cs}_{0.9}\text{Al}_{0.9}\text{Si}_{2.1}\text{O}_6$  sintered body with 94.5% relative density.

ior in the temperature range of 298 to ca. 473 K was also recognized in  $\text{Cs}_{0.9}\text{Al}_{0.9}\text{Si}_{2.1}\text{O}_6$  powder.<sup>7)</sup>

#### 4. Conclusions

A dense cubic  $\text{Cs}_{0.9}\text{Al}_{0.9}\text{Si}_{2.1}\text{O}_6$  sintered body was fabricated from the green body of calcined powders prepared by heating mixed raw materials of  $\text{Al}_2\text{O}_3/\text{SiO}_2$  fine powder and

CsNO<sub>3</sub> powder. The results are as follows:

(1) A calcined powder with the amorphous phase with a slight amount of CsNO<sub>3</sub> was synthesized by calcination of mixed raw materials of Al<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub> fine powder and CsNO<sub>3</sub> powder at 798 K for 20 h in air.

(2) A dense cubic Cs<sub>0.9</sub>Al<sub>0.9</sub>Si<sub>2.1</sub>O<sub>6</sub> sintered body with a 94.5% relative density was fabricated by heating the green body of a 798 K-calcined powder at 1673 K for 20 h in air.

(3) The dense cubic Cs<sub>0.9</sub>Al<sub>0.9</sub>Si<sub>2.1</sub>O<sub>6</sub> sintered body exhibited linear and low thermal expansion property of which the thermal expansion rate was ca. 0.13% (TEC:  $1.3 \times 10^{-6}/K$  (298–1273 K)) at 1273 K.

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