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Journal of the European Ceramic Society 26 (2006) 475–479
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Effects of PMMA on porous structure of pollucite

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Abstract

The effects of PMMA as a pore-forming reagent and the powder for Cs-deficient pollucite, $Cs_9Al_{0.9}Si_{2.1}O_6$, calcined at 1073 K, on the microstructure of the porous body of $Cs_{0.9}Al_{0.9}Si_{2.1}O_6$ were investigated. The $Cs_{0.9}Al_{0.9}Si_{2.1}O_6$ porous bodies were fabricated by sintering the green compacts of the calcined powder and PMMA adding 35 mass% to the calcined powder. When the green compact was heated at 873 K in air for 20 h, pores <1 μm were observed in the porous body, suggesting that the PMMA previously dissolved in acetone was uniformly distributed in the calcined powder by the ball milling. The pore size of the obtained porous structure increased with increasing the size of the aggregated particles and the pore size distribution was significantly related to the size of Al_2O_3 balls and the time for the ball milling for mixing the calcined powders and PMMA.

Keyword: Pollucite

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1. Introduction

Pollucite, $CsAlSi_2O_6$, a zeolite-related compound with cubic symmetry, has a three-dimensional aluminosilicate framework structure composed of 48 $(Si,Al)O_4$ tetrahedra with 16 Cs+ ions occupying large 12-coordinated cavities in the unit cell,[1,2] and recently, we found that cubic Cs-deficient pollucite, $Cs_{0.9}Al_{0.9}Si_{2.1}O_6$, showed a lower thermal expansion than $CsAlSi_2O_6$ with a linear thermal expansion coefficient (TEC) was ca. $2.05 \times 10^{-6}/K$[3,4] in the temperature range of 298–1273 K.

Considering the high-melting point >2173 K[5] and the low TEC of $Cs_{0.9}Al_{0.9}Si_{2.1}O_6$ with cubic symmetry, it would make it an attractive candidate material for high-temperature–high-thermal shock structural applications, such as combustors and nozzle flaps for turbines in jet aircrafts.[6] The materials do not have a serious problem that microcracks arise from thermal stress due to anisotropic thermal expansion such as the cordierite having an issue that microcracks occur during regeneration.[7]

Porous materials with high-melting point and low-thermal expansion property could be applied for air filters under higher temperatures. In our previous study,[8] cubic $Cs_{0.9}Al_{0.9}Si_{2.1}O_6$ porous bodies with submicron-pores were fabricated using the $Cs_{0.9}Al_{0.9}Si_{2.1}O_6$ calcined powders and PMMA as a pore-forming reagent. Consequently, it was found that the $Cs_{0.9}Al_{0.9}Si_{2.1}O_6$ porous body with 0.37 μm in pore size and 48.4% in porosity could be fabricated by heating the green compact consist of the calcined powder and PMMA at 1673 K in air for 20 h. The porous body could be a candidate for filtering fine particles with a diameter <1 μm arising from the secondary combustion products from vehicular traffic and energy production.[9–11]

However, effects of PMMA and the calcined powder on the microstructure of the $Cs_{0.9}Al_{0.9}Si_{2.1}O_6$ porous body have not been studied in detail. In this study, importance of dispersion of PMMA and ball milling of the calcined powder for the porous structure of the sintered bodies has been mainly examined by a scanning electron microscopy and an Hg-intrusion method.

2. Experimental

2.1. Synthesis of $Cs_{0.9}Al_{0.9}Si_{2.1}O_6$ powder

$CsNO_3$ powder (99% up; Koujyundo Kagaku Co. Ltd., Japan), Al_2O_3 sol (Alumina sol 200; Nissan Kagaku Co. Ltd.,

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doi:10.1016/j.jeurceramsoc.2005.07.011

Japan) and SiO_2 sol (Snotex O; Nissan Kagaku Co. Ltd., Japan) were used as starting raw materials. Firstly, Al_2O_3 and SiO_2 sols were mixed at pH 5.4, dried, and heated at 873 K in air for 20 h to obtain the mixed fine powders of γ-Al_2O_3 and amorphous SiO_2 (molar ratio of Al/Si = 0.9/2.1).[12] Secondly, $CsNO_3$ powders were added to the fine powder mixtures of γ-Al_2O_3 and amorphous SiO_2 to give the molar ratio of 0.9/2.1 for Cs/Si. The mixed powders were heated at 873 K in air for 20 h to decompose $CsNO_3$. And then the powders consisting of amorphous phase were calcined at 1073 K in air for 20 h to crystallize the pollucite phase in the calcined powder.[8]

2.2. Fabrication of $Cs_{0.9}Al_{0.9}Si_{2.1}O_6$ porous body

The powders calcined at 1073 K were well dispersed in acetone by an ultrasonic treatment. Then, the calcined powders and polymethyl methacrylate (PMMA; $(C_5H_8O_{12})_n$, Wako Co. Ltd., Japan) were mixed in acetone for 24 h by ball milling. The Al_2O_3 balls used for the ball milling were 5 and 15 mm Ø. Additive ratio of PMMA to the calcined powders was 35 mass% of which the value was previously optimized.[8] Green compacts composed of the calcined powders and 35 mass%-PMMA were prepared by anisotropic pressing at 49 MPa for 1 min, followed by cold isostatic pressing (CIP) at 196 MPa for 1 min. The specimen size was approximately 5 mm × 5 mm × 10 mm. The prepared compact was heated at 873 K in air for 20 h to decompose PMMA at the heating rate of 2 K/min. Then the pre-heated specimens were sintered at temperatures ranging from 1373 to 1673 K in air for 20 h.

2.3. Evaluations

Thermal decomposition behavior for PMMA, PVA (polyvinyl alcohol; Wako Co. Ltd., Japan), and PVB (polyvinyl butyral 300; Wako Co. Ltd., Japan) mixed in the pollucite powders were investigated by thermogravimetry and differential thermal analysis (TG–DTA; TAS200, Rigaku Co. Ltd., Japan). Particle size distributions for the calcined powders were estimated using the lineal intercept method by counting 200 particles in photographs by a scanning electron microscope (SEM; S-4100, Hitachi Co. Ltd., Japan).

Crystalline phases in the fabricated $Cs_{0.9}Al_{0.9}Si_{2.1}O_6$ porous bodies were examined by X-ray diffraction apparatus (XRD; Rad-B, Rigaku Co. Ltd., Japan, Cu Kα, 40 kV, 30 mA). Fractured surfaces of the porous bodies were observed using the SEM. Porosity and pore size distribution for the porous bodies were investigated using Hg-intrusion porosimetry (Autopore 9520, Shimadzu Co. Ltd., Japan).

3. Results and discussion

3.1. Thermal decomposition of PMMA in the green compact

Thermal decomposition behaviours of various organic polymers such as PMMA, PVA, and PVB were investigated by TG–DTA. Mixtures of the organic polymers and the pollucite-powder were used as samples for TG–DTA. The result the case of PMMA is shown in Fig. 1. The mass decrease curve and the endothermic peak were observed, and any other change for the mass and the heat was not observed. Therefore, it was found that the thermal decomposition of PMMA occurred in the temperature range of ca. 523–573 K, which was narrower and lower than the case of PVA (range ca. 373–773 K) and PVB (range 473–873 K). Therefore, PMMA was applied for fabrication of the porous body of $Cs_{0.9}Al_{0.9}Si_{2.1}O_6$.

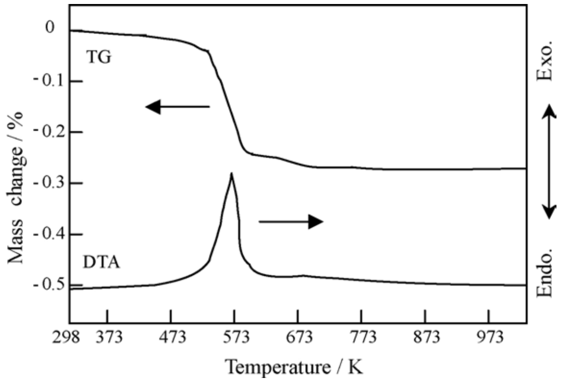

Fig. 1. TG–DTA curve for the mixture of the powder calcined at 1073 K and 35 mass%-PMMA.

Morphology of the powder calcined at 1073 K is shown in the SEM image of Fig. 2. Aggregated particles <1 μm in diameter were mainly observed. Here, the adding ratio of PMMA to the calcined powder was 35 mass%.[8] The green compact was fabricated using the mixture of the powder calcined at 1073 K and 35 mass%-PMMA, which was previously prepared by mixing the calcined powder and PMMA using ball milling, with Al_2O_3 balls of 5 mm Ø. Then PMMA in the green compact was heated at 873 K for

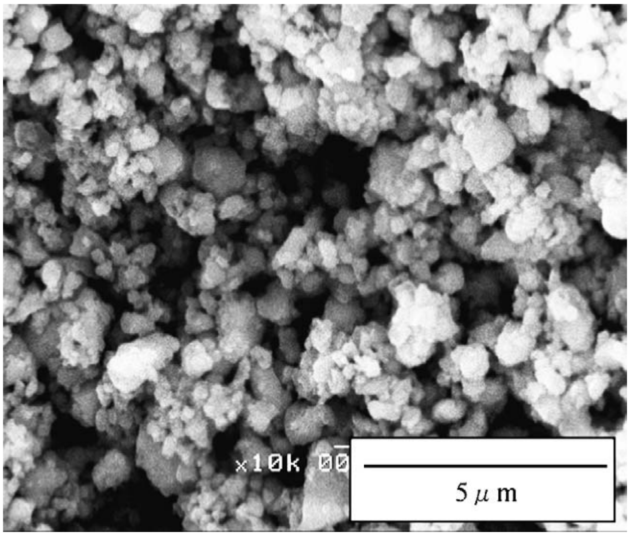

Fig. 2. SEM morphology of the powder prepared by heating the mixtures of the calcined powder and 35 mass%-PMMA at 1073 K for 20 h.

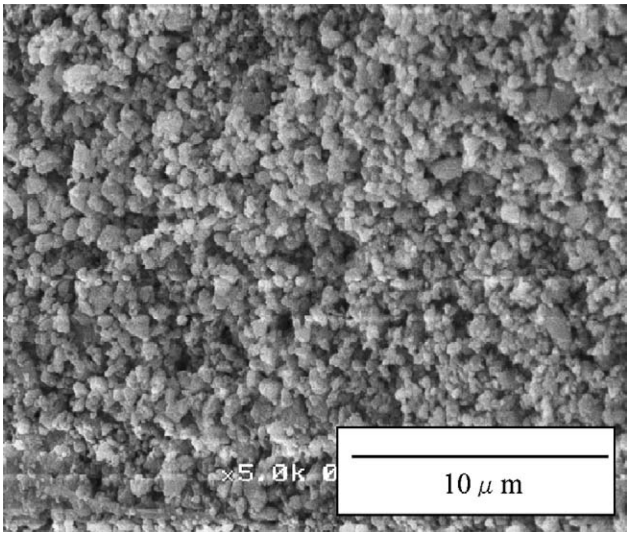

Fig. 3. SEM image of the fractured surface for the specimens obtained by heating the green compact of the calcined powder and PMMA at 873 K for 20 h.

20 h at the heating rate of 2 K/min[8] in order to decompose PMMA.

SEM image for the fractured surface of the specimen obtained by heating the green compact at 873 K for 20 h is shown in Fig. 3. Grains with diameter <1 μm and the pores among the grains were observed. The grain size was almost corresponded with the aggregated particle size, suggesting that PMMA dissolved in acetone was well dispersed among the aggregated particles during the process of mixing the calcined powder and PMMA. Therefore, it was considered that the pores in the specimens were derived from the thermal decomposition of PMMA in the green compact.

3.2. *Fabrication of porous structure of pollucite*

XRD patterns for the surfaces of the specimens sintered at temperatures ranging from 1373 to 1673 K are shown in Fig. 4. Crystallinity for the pollucite phase increased with increasing the sintering temperature, although unknown peak was recognized at 1373 and 1473 K. The single phase of pollucite was obtained above 1573 K. In this way, single phase of $Cs_{0.9}Al_{0.9}Si_{2.1}O_6$ was well crystallized through the heating process for the green compact of PMMA and the calcined powder including an amorphous phase.

SEM image for the fractured surface of the specimen sintered at 1673 K for 20 h is shown in Fig. 5a. From the result that grains and pores in the specimens became larger than after PMMA removal at 873 K, it was clarified that the grain growth and the pore formation are caused by increasing the heating temperature, However, the pores in the specimen disappeared due to glass formation on the surface of the specimen at a higher temperature, 1773 K. Pore size distribution for the fractured surface of the specimen is shown in Fig. 5b. Pore size was in the range of ca. 0.2–7 μm, and the main

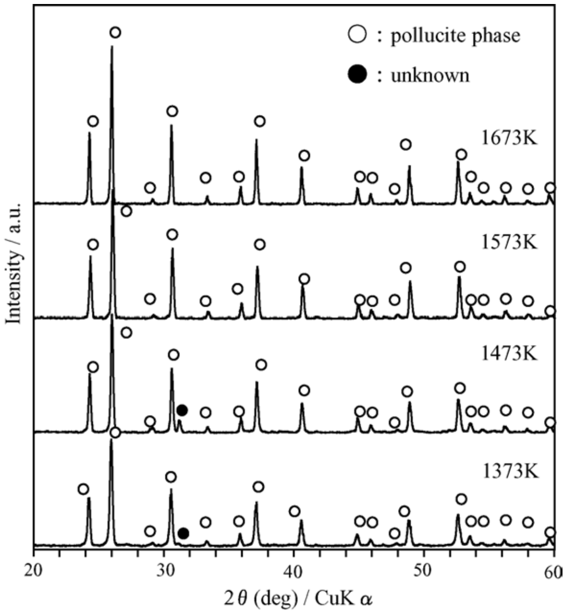

Fig. 4. XRD patterns for the specimens for $Cs_{0.9}Al_{0.9}Si_{2.1}O_6$ prepared by heating green compact at temperature range of 1373–1673 K.

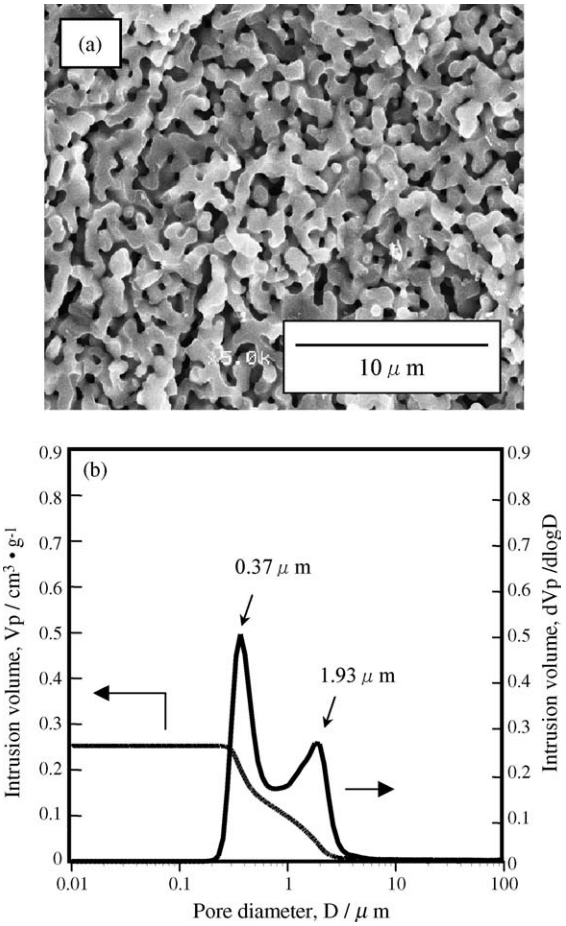

Fig. 5. SEM image of the fractured surface (a) and pore size distribution (b) of the $Cs_{0.9}Al_{0.9}Si_{2.1}O_6$ porous body fabricated from the mixture of the calcined powder and PMMA prepared using Al_2O_3 balls with 5 mm Ø for 48 h.

Table 1
Effect of size of Al_2O_3 balls and time for the ball milling on the size of the aggregated particles, pore size distribution, and porosity

	Aggregated particles (μm)	Pore size distribution	Porosity (%)
I[8]	0.9–1.3	0.37 1.93	48.5
II	1.7–2.6	0.37 2.60	54.9
III	2.2–3.4	0.68 3.60	53.6

Condition I: 5 mm Ø Al_2O_3 balls, 48 h; condition II: 5 mm Ø Al_2O_3 balls, 24 h; condition III: 15 mm Ø Al_2O_3 balls, 24 h.

pore sizes were 0.37 and 1.93 μm. The grain size was in the range of ca. 1–2 μm, which corresponded with that for the specimen heated at 873 K for 20 h to decompose PMMA. The result suggests that the grains in the specimens sintered without significant grain growth. The peaks for the pore size seem to be due to the difference in the degree of the aggregation of the particles in the calcined powders.

3.3. Enlargement of the pore size in the porous body

Influence of the size of Al_2O_3 balls used for the ball milling on the pore size in the $Cs_{0.9}Al_{0.9}Si_{2.1}O_6$ porous bodies was investigated by changing the size of the Al_2O_3 ball used in the process for mixing the calcined powders and PMMA. The ball size was changed from 5 to 15 mm Ø in this experiment.

The green compact prepared using the mixture of the calcined powders and 35 mass%-PMMA, which were mixed using the Al_2O_3 balls with 15 mm Ø for 24 h, were heated at 873 K for 20 h to decompose PMMA, then sintered at 1673 K for 20 h. The heating condition was the same with the green compact of the calcined powder prepared using the Al_2O_3 balls with 5 mm. SEM image of the fractured surface of the fabricated $Cs_{0.9}Al_{0.9}Si_{2.1}O_6$ porous body using the Al_2O_3 balls with 15 mm Ø is shown in Fig. 6a. The pore size and the grain size in the porous body were larger than those for the case of 5 mm Ø Al_2O_3 balls. The porosity of the fabricated porous body was 53.6%. Pore size distribution for the porous body is shown in Fig. 6b. The pore size was in the range of ca. 0.3–10 μm, and the main pore sizes were 0.68 and 3.60 μm. The range of the pore size was larger and the main pore sizes remarkably increased in comparison with the case of 5 mm Ø Al_2O_3 balls. From the result, it was found that increasing the size of the Al_2O_3 ball was effective for enlargement of the pore size in the $Cs_{0.9}Al_{0.9}Si_{2.1}O_6$ porous body.

The particle size distribution in the calcined powder, the pore sizes and the porosities in the $Cs_{0.9}Al_{0.9}Si_{2.1}O_6$ porous bodies are shown in Table 1. In the case of conditions I[8] and II, the ball milling with the Al_2O_3 balls of 5 mm Ø was performed for 48 and 24 h, respectively. The sizes of the aggregated particles and the pores increased as the time for the ball milling decreased. In the case of condition III, the ball milling with the Al_2O_3 balls of 15 mm Ø was performed for 24 h. The sizes of the aggregated particles and the pores further enlarged as compared with the case of conditions I and II. On the other hand, decreasing the ball milling time was more effective for increasing the porosity than the enlargement of the Al_2O_3 ball size.

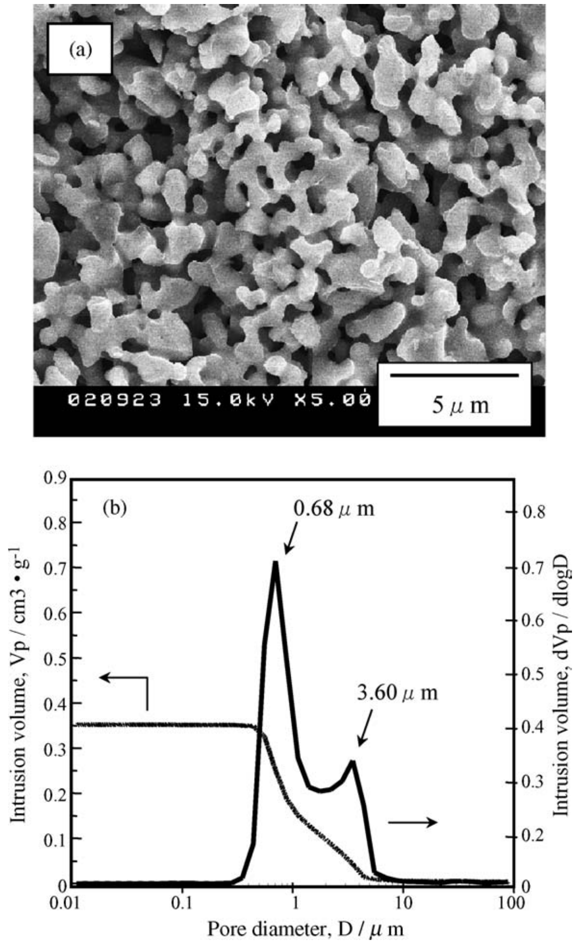

Fig. 6. SEM image of the fractured surface (a) and pore size distribution (b) of the $Cs_{0.9}Al_{0.9}Si_{2.1}O_6$ porous body fabricated from the mixture of the calcined powder and PMMA prepared using Al_2O_3 balls with 15 mm Ø for 24 h.

From the above result, it was clarified that enlargement of the size of Al_2O_3 balls and increasing of the time of the ball milling prevented decreasing the size of the aggregated particles. That is, it was considered that the difference in the amount of the aggregated particles resulted in the changing for the pore size in the $Cs_{0.9}Al_{0.9}Si_{2.1}O_6$ porous bodies, and it would be important for the enlargement of the pore size to optimize the ball milling time and the Al_2O_3 ball size, besides the dispersion of PMMA in the calcined powder should be considered.

4. Conclusions

$Cs_{0.9}Al_{0.9}Si_{2.1}O_6$ porous bodies were fabricated by heating the green compacts of the powder calcined at 1073 K and

35 mass%-PMMA to clarify the influence of PMMA and the calcined powder on the porous structure. Consequently, it was found that the microstructure of the porous bodies with single phase of $Cs_{0.9}Al_{0.9}Si_{2.1}O_6$ was influenced by the condition of the ball milling in the process of mixing the calcined powder and PMMA. When the ball milling was performed using the Al_2O_3 balls with 15 mm Ø for 24 h, a $Cs_{0.9}Al_{0.9}Si_{2.1}O_6$ porous body with the main pore sizes 0.68 and 3.60 μm was fabricated due to the enlargement of the aggregated particles.

Acknowledgements

This work was partially supported by Grant-in-Aids No. 17750192 for Science Research from the Ministry of Education, Culture, Sports, Science and Technology of Japan, and by Mukai Science and Technology Foundation in Japan.

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