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Study of low-thermal-expansion porcelain employing petalite and β -eucryptite

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Clay mixtures with petalite or β -eucryptite were studied with the aim of obtaining thermal shock resistant porcelain. β eucryptite was synthesized by mixing Li₂CO₃ and Al(OH)₃ with silica in stoichiometric compositions, and the synthesized β eucryptite showed a thermal expansion coefficient of $-7.10 \times 10^{-6/9}$ C. The final phase and coefficient of thermal expansion of the fired petalite-clay and eucryptite-clay samples were examined according to changes of the mixing ratio and firing temperature. In the petalite-clay samples, lithium alumina silicate (Li₂O · Al₂O₃ · 7.5SiO₂) and keatite-type β -spodumene, which shows a positive thermal expansion coefficient, were observed. In the eucryptite-clay samples, β -quartz-type β spodumene was well developed according to the increase of eucryptite content and firing temperature. Under the conditions of 70 wt% eucryptite content and at a firing temperature of 1350 °C, the eucryptite-clay sample yielded a low thermal expansion coefficient of 0.7 × 10^{-6/9}C. The mixing of β -eucryptite into clay enabled the realization of excellent thermal shock resistant porcelains.

Key words: Thermal Expansion, β -eucryptite, Petalite, β -spodumene, Thermal shock resistance.

Introduction

In general, LAS (Li₂O-Al₂O₃-SiO₂) materials are known to have low thermal expansion coefficients. In particular, β -spodumene (Li₂O · Al₂O₃ · 4SiO₂) and β eucryptite ($Li_2O \cdot Al_2O_3 \cdot 2SiO_2$) are the representative crystal structures of LAS system showing low thermal expansion coefficients. Since many researchers have reported that β -eucryptite displays negative thermal expansion behavior, studies on LAS (Li₂O-Al₂O₃-SiO₂) materials have been actively conducted [1-3]. Gaillery et al. [4] examined the thermal expansion anisotropy of β eucryptite crystals through an XRD study and Roy et al. [5] identified for the first time that the irreversible $\alpha \rightarrow \beta$, transition of eucryptite occurred by a hydrothermal reaction at 972 °C. They later reported that petalite $(Li_2O \cdot Al_2O_3 \cdot 8SiO_2)$, which also belongs to the LAS family, was transformed into β -spodumene under a temperature range of 700 ~ 950 °C, and studies upon the application of petalite to thermal resistant materials subsequently have been actively carried out. Fishwick et al. [6, 7] reported low thermal expansion characteristics of mixed compositions of spodumene, petalite, and kaolin. In particular, among studies on thermal resistant porcelains, research focused on improving thermal shock resistibility through a reduced coefficient of thermal expansion by inducing a β -spodumene crystal phase with the addition of petalite has been performed.

However, there have been few studies on materials belonging to eucryptite-clay systems. While several studies [8-10] on the synthesis methods of β -spodumene such as solid phase synthesis, coprecipitation, sol-gel transition, etc. have been conducted, few studies on the synthesis of eucryptite have been reported.

In this study, the crystallization behavior and physical and thermal properties of porcelain prepared by adding petalite and synthesized eucryptite to clay were examined. Through the design of the porcelain composition it was anticipated that thermal resistant ceramics having a minimized thermal expansion coefficient to maximize thermal shock resistance could be obtained. The β eucryptite powder used for the present study was synthesized by adding lithium carbonate (Li₂CO) and aluminum hydroxide (Al(OH)₃) to silica (SiO₂), and the properties of the synthesized β -eucryptite were also examined.

Experimental Procedure

Raw materials

'Kimchun' silica(mean particle size: $3 \mu m$) was employed to prepare the β -eucryptite, and aluminum hydroxide (Al(OH)₃, 99.7%, KC Ltd. Korea) was used to supplement the insufficient alumina. Lithium carbonate (Li₂CO₃, 99.8%, Wako Pure Chemical Industries Ltd., Japan) was used as a source material for the lithium. Petalite imported from Zimbabwe was used, and kaolinitic Gairome clay was employed to obtain the required plasticity for the green body. Results of a chemical analysis on each material are summarized in Table 1.

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	SiO ₂	Al_2O_3	Fe ₂ O ₃	TiO ₂	CaO	MgO	K ₂ O	Na ₂ O	Li ₂ O	F	Ig.loss	Total
Petalite	76.16	17.24	0.18	0.03	0.21	0.24	0.39	0.16	4.49	0.11	0.80	100.01
Gairome	50.19	33.53	1.26	0.79	0.18	0.29	0.91	0.01	0.00	0.00	12.84	100.00
Kimchun silica	99.60	0.00	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.37	100.00
Li ₂ CO ₃	_	_	_	-	_	_	-	_	40.46	_	59.54	100.00
Al(OH) ₃	_	65.36	_	_	_	_	_	_	_	_	34.64	100.00

Table 1. Chemical analysis of raw materials (wt%).

Preparation of β-eucryptite powder

Lithium carbonate, aluminum hydroxide, and silica powder were mixed together according to the batch composition ratio listed in Table 2 to match the composition of *β*-eucryptite. Detailed ball milling conditions to prepare the mixtures are presented in Table 3. Isopropyl alcohol was used as grinding solvent media instead of water due to the water solubility (about 1.34 g/100g.H₂O) of lithium carbonate. The slurry mixture was filtered through a standard 200 mesh sieve and dried at 110 °C for 24 h, and then crushed and heat treated at 1000 °C, 1100 °C, 1200 °C, and 1300 °C for 90 min with a 5 °C/min heating rate. The crystal phase of the heat treated powders was examined by using X-ray diffractometry (Rigaku 2200, Tokyo, Japan). The green compacts of the β -eucryptite powders were then heat treated at 1300 °C for 2 h to examine the thermal expansion behavior. A dilatometer (DIL 402C, Netzswch, Germany) was used for the thermal expansion test. The microstructure of the prepared specimen was observed by using a scanning electron microscope (SEM, 3500N/Hitachi, Japan).

Preparation of heat-resistant-porcelain specimens

Green bodies of petalite-clay and eucryptite-clay were sintered and then the thermal expansion properties and crystalline phases were examined. To make the green bodies, Gairome clay was mixed with petalite and synthesized eucryptite, respectively [11]. In the forming process, the clay was mixed at over

Table 2. Batch ratio of eucryptite.

Raw material	Weight (%)	Component	Weight (%)	Mole (%)
Kimchun silica	34.34	SiO ₂	47.6	49.91
Al(OH) ₃	44.54	Al_2O_3	40.51	25.05
Lithium carbonate	21.11	Li ₂ O	11.89	25.04

Table 5. Dan mining conditions.	Table 3.	Ball	milling	conditions.
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Vol. of jar	1,000 cc, epoxy resin
Size of ball	5 mm of diameter, zirconia ball
Vol. of loading ball	550 cc, 3.35 g/cc of bulk density
Load of materials	300 g
Load of solvent	500cc of iso-propyl alcohol
Milling time	72 h

Table 4. Composition of each specimens (wt%).

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	PB-1	PB-2	PB-3	PB-4	EB-1	EB-2	EB-3	EB-4
Petalite	40	50	60	70	0	0	0	0
Synthetic eucryptite	0	0	0	0	40	50	60	70
Gairome clay	60	50	40	30	60	50	40	30

30 wt% in order to retain formability. The composition ratios of each sample are listed in Table 4. The ball milling conditions to prepare the slurry are presented in Table 3. Subsequently, 1cc of a deflocculant (sodium silicate solution) was mixed into each slurry. The resulting clay was slip-casted by using a plaster mold. Casted specimens were then completely dried and then heat treated at 1200 °C, 1250 °C, 1300 °C, and 1350 °C for 3 h with a 5 °C/min heating rate. The crystal phase of the sintered samples was examined and the thermal expansion coefficient was measured in a range of 30 °C ~ 1,250 °C

Results and Discussion

Characteristics of β -eucryptite powder

The development of the crystalline phase of the synthesized β -eucryptite powder is illustrated in Fig. 1. Three phases of β -eucryptite, α -quartz, and lithium silicate (Li2SiO3, Li2OSiO2) were observed at 900 °C At this temperature, the crystallinity of β -eucryptite was very low, and it was found that free silica and α quartz co-existed. The lithium reacted with silica and formed an intermediate phase of β -eucryptite (Li₂SiO₃). The lithium silicate phases disappeared upon exceeding temperature of 1000 °C and the XRD intensity of β eucryptite increased rapidly, enabling the existence of a single β -eucryptite phase. The surface microstructure of the β -eucryptite powder compact heated at 1300 °C is presented in Fig. 2. The grains were irregularly shaped with a wide size distribution and some liquid phases, micro-cracks, and pores were also observed. It is assumed that the cracks appeared due to thermal expansion anisotropy in the densified *β*-eucryptite polycrystals. The thermal expansion behavior of the sintered specimen is presented in Fig. 3. From room temperature up to 1250 °C, it showed negative thermal expansion behavior, and the measured coefficient of



Fig. 1. XRD patterns of synthesized β -eucryptite powders sintered at various temperatures for 4 h.



Fig. 2. SEM micrograph of β -eucryptite specimen sintered at 1300 °C for 2 h.



Fig. 3. Themal expansion of synthesized β -eucryptite powder compact sintered at 1300 °C for 2 h.

thermal expansion was $-7.10 \times 10^{-6/\circ}$ C.

Characteristics of petalite-clay and eucryptite-clay specimens

Crystallization

The results of the observed crystallite phases and the measured thermal expansion coefficient of each specimen are summarized in Table 5 in accordance with heating temperature. In the petalite-clay samples, mullite, α -quartz, and cristobalite phases were observed at 1200 °C.

The transition to cristobalite phase at relatively low temperature corresponds to the theoretical mechanism reported by Brandley et al. [12] where the Li⁺ ions work as a network modifier to cut the crystal lattice of the α -quartz structure and enable easy rearrangement to form the cristobalite. Lithium alumina silicate $(Li_2O \cdot Al_2O_3 \cdot 7.5SiO_2)$, mullite, and cristobalite were observed at 1250 °C. The lithium alumina silicate is a prior phase of β -spodumene solid solution, and the α quartz disappeared because of the transition to cristobalite. At petalite content of 70 wt% at 1300 °C, and petalite content of 60 wt% and 70 wt% at 1350 °C, keatite-type β -sodumene was observed. Li *et al.* [13] reported that the β -spodumene solid solution in a LAS composition exists either as β -quartz-type or keatitetype. The β -quartz-type spodumene having a similar structure with general β-spodumene showed negative thermal expansion behavior with a stable crystal structure. The β -quartz-type spodumene would transition to a keatite solid solution with an increase of heat treatment temperature and time. Upon this transition, bonds of the crystal lattice of β -quartz are broken and then rearranged. The keatite solid solution is known to be a less stable crystal structure and displays positive thermal expansion. The petalite-clay samples were crystallized to keatite-type spodumene as the heating temperature and petalite content increase. The β eucryptite-clay samples showed mullite and cristobalite phases at 1200 °C, and when the content of eucryptite was increased to 60 wt%, the lithium alumina silicate phase was observed with the two phases. Mullite and βquartz-type spodumene were formed at 1250 °C, and with increased temperatures of 1300 °C and 1350 °C, these phases continued to exist. The peak strength of the β-spodumene was significantly increased with eucryptite content exceeding 60 wt% at 1350 °C, but the peak strength of mullite tended to decrease gradually. From these results, it was estimated that the formation of β -spodumene would increase with an increase of eucryptite content in the clay mixture at high firing temperature. The EB-3 and EB-4 samples showed low thermal expansion coefficients with an increase of the peak intensity of β -spodumene.

Density and absorption

The apparent densities were expected to increase at 1200 °C as the clay content increased, but the increase of density was more affected by the content of LAS materials from temperature of 1250 °C. The densification improved at higher temperature by the formation of a liquid phase derived from the LAS materials. In the eucryptite-clay samples, the densities were higher than those of the petalite-clay samples because of the enhancement of liquid phase sintering according to the Li₂O amount in the LAS materials. In particular, the EB-3 and EB-4 samples showed very low absorption, below 1%, with improved density. This indicates that a



Fig. 4. Effect of LAS materials content on coefficient of thermal expansion of clay mixtures fired at 1200 °C.



Fig. 5. Effect of LAS materials content on coefficient of thermal expansion of clay mixtures fired at 1250 °C.

dense porcelain having an absorption of almost 0% with high thermal shock resistance can be fabricated by controlling the β -eucryptite content and heat temperature.

Coefficient of thermal expansion

The variation of the thermal expansion coefficient of the petalite-clay and eucryptite-clay samples is illustrated in Figs. 4 to 7 at each temperature. At the relatively low firing temperature of 1200 °C (Fig. 4), the thermal expansion coefficient showed a relatively slow decrease as the petalite and eucryptite content increased. This is due to the thermal expansion caused by the main crystalline phases of α -quartz and cristobalite. At temperature of 1250 °C (Fig. 5), a rapid decrease of the thermal expansion coefficient was observed in the eucryptite-clay samples with over 50 wt% eucryptite content. This is caused by the formation of β -spodumene. However, in the case of petalite-clay samples, the thermal expansion coefficient decreased slowly. This is attributed to



Fig. 6. Effect of LAS materials content on coefficient of thermal expansion of clay mixtures fired at 1300 °C.



Fig. 7. Effect of LAS materials content on coefficient of thermal expansion of clay mixtures fired at 1350 °C.

the remaining cristobalite and lithium alumina silicate (Li₂O · Al₂O₃ · 7.5SiO₂). At firing temperature of 1300 °C (Fig. 6), the thermal expansion coefficient of the eucryptiteclay samples significantly reduced to $1.5 \sim 1.0 \times 10^{-6/\circ}$ C as the eucryptite content was increased. This is due to sufficient development of the β -spodumene crystal phase. In contrast, the thermal expansion coefficient of the petalite-clay samples with 60 wt% petalite content showed a relatively small decrease and the gap between the two coefficients gradually increased. At firing temperature of 1350 °C (Fig. 7), a very low thermal expansion coefficient close to 0 $(0.7 \times 10^{-6})^{\circ}$ C) was measured for eucryptite content of 70 wt%. This is due to the disapperance of the mullite phase and enhanced development of the β -spodumene crystal phase, which caused a reduction of the thermal expansion coefficient, as seen from the XRD analysis results listed in Table 5. In the case of the petalite-clay samples, the thermal expansion coefficient decreased slowly even with 70 wt% content. From these results, it is estimated that

	1200 °C		1250 °C		130	0 °C	1350 °C	
Sample	XRD	CTE (× 10 ^{-6/°} C)	XRD	CTE (× 10 ^{-6/°} C)	XRD	CTE (× 10 ^{-6/°} C)	XRD	CTE (× 10 ⁻⁶ / ⁰ C)
PB-1	Μ, C, αQ	3.3	LAS,M, C	3	LAS,M, C	2.9	LAS,M, C	2.8
PB-2	Μ, C, αQ	3	LAS,M, C	2.8	LAS,M, C	2.7	LAS,M, C	2.7
PB-3	Μ, C, αQ	2.9	LAS,M, C	2.7	LAS,M, C	2.4	LAS,M, Ks	2.3
PB-4	Μ, C, αQ	2.7	LAS,M, C	2.6	LAS,M, Ks	2.2	LAS,M, Ks	2.1
EB-1	М, С	2.7	βs, M	2.5	βs, M	2	βs, M	1.8
EB-2	М, С	2.5	βs, M	2.3	βs, M	1.5	βs, M	1.5
EB-3	LAS, M, C	2.3	βs, M	2	βs, M	1.3	$\beta s(s),M(w)$	1
EB-4	LAS, M, C	2	βs, M	1.5	βs, M	1	$\beta s(s), M(w)$	0.7

Table 5. Crystalline Phases and thermal expansion coefficients of petalite-clay and eucryptite-clay specimens at different firing temperatures.

 $LAS = Li_{2}O \cdot Al_{2}O_{3} \cdot 7.5SiO_{2}, \\ \beta s = \beta - Spodumene, \\ M = Mullite, \\ \alpha Q = \alpha - Quartz, \\ Ks = Keatite solid solution, \\ C = Cristobalite, \\ W = weak, \\ S = strong. \\ S =$

Table 6. Physical properties of petalite-clay and eucryptite-clay specimens.

	1200 °C		1250 °C		1300	0 °C	1350 °C	
Sample No.	Water absorption (%)	Apparent density (g/cm ³)						
PB-1	11.58	2.49	10.81	2.47	6.91	2.50	5.41	2.52
PB-2	11.80	2.49	10.54	2.50	6.90	2.49	5.13	2.54
PB-3	12.62	2.46	9.95	2.51	6.47	2.53	5.02	2.55
PB-4	13.25	2.45	8.76	2.53	5.94	2.54	4.19	2.56
EB-1	10.21	2.52	7.68	2.52	5.06	2.55	3.15	2.61
EB-2	11.23	2.49	6.87	2.55	4.53	2.57	2.59	2.60
EB-3	11.59	2.48	5.68	2.57	0.91	2.55	0.89	2.60
EB-4	12.08	2.47	4.32	2.57	0.39	2.59	0.05	2.60

it would be impossible to reduce the thermal expansion coefficient below $2.0 \times 10^{-6/\circ}$ C with samples made from a petalite-clay mixture. On the other hand, it is believed that the eucryptite-clay samples would have a thermal expansion coefficient close to zero.

Conclusions

Porcelains having excellent thermal shock resistant properties were studied by applying materials having low thermal expansion properties such as β -eucryptite and petalite. The conclusions obtained from examination of the thermal expansion properties and crystalline phases in petalite-clay and eucryptite-clay samples are as follows:

 β -eucryptite powder was synthesized from silica and lithium carbonate with an aluminum hydroxide mixture in a stoichiometric composition. The β -eucryptite phase was observed from firing temperature of 900 °C, and a well developed single phase of β -eucryptite was observed beyond firing temperature of 1000 °C. The measured thermal expansion coefficient of the synthesized β -eucryptite was -7.10×10^{-6} /°C.

In the petalite-clay samples, lithium alumina silicate $(Li_2O \cdot Al_2O_3 \cdot 7.5SiO_2)$ which is a prior phase of β -

spodumene was observed as a major crystal phase, and a keatite-type β -spodumene solid solution, which shows a positive thermal expansion coefficient, was formed with an increase in petalite content at high temperature. These findings suggest there is a limit to how low the thermal expansion coefficient of petalite-clay samples can be reduced.

In the case of the eucryptite-clay samples, β -quartztype β -spodumene, which shows a negative thermal expansion coefficient, was observed as the major crystal phase with mullite from a firing temperature of 1250 °C. The thermal expansion coefficient of the eucryptite-clay samples decreased continuously along with an increase of the eucryptite content and firing temperature, enabling a low thermal expansion coefficient of 0.7×10^{-6} /°C. It was estimated that a thermal expansion coefficient close to zero would be available by adding eucryptite to clay for fabrication of excellent thermal resistant porcelains.

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