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Synthesis of low thermal expansion ceramics prepared from pyrophyllite and lithium source

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In this study, the low thermal expansion ceramic, petalite $(Li_2O \cdot Al_2O_3 \cdot 8SiO_2)$, was synthesized by using pyrophyllite, and their characteristics were examined. Pyrophyllite is consisted of SiO₂ and Al₂O₃, which are the main component of petalite. For the synthesis of petalite, Li_2CO_3 or $LiOH \cdot H_2O$ were used as a source of Li_2O . In the mixing ratio of 6.7 : 1 wt% (pyrophyllite : Li_2CO_3), fully crystallized petalite was synthesized, and the powder compacts were densified at 1150 °C. Some Li compounds, which have low melting point, caused a formation of liquid phase in the densified samples. The petalite phase was transformed to β -spodumene during heating process, and the sintered petalite showed a negative thermal expansion coefficient of -0.43×10^{-6} °C. Finally, the experimental results showed that the pyrophyllite is an expected material for the synthesis of low thermal expansion ceramics.

Key words: Pyrophyllite, Petalite, Thermal expansion coefficient, Lithium carbonate, β -spodumene.

Introduction

Ceramic materials are characterized with excellent inherent properties, such as high hardness, high corrosion resistance, and high thermal resistance that attracted researchers delved into ways of practical applications exploiting such excellent properties. In particular, the ceramic materials having excellent thermal resistance attributable to their low thermal expansion coefficients have been used in diverse applications including heat resistant table wares, stoves, sight glass of gas fire ovens, heat exchangers, and in refractories [1, 2].

In general, ceramic materials which are characterized with low thermal conductivity would experience the large internal stress induced by significant thermal gradient generated by rapid temperature change. In cases of ceramic materials experiencing rapid temperature decrease, they would be exposed to the tensile stress induced thereby and the ceramic materials having low tensile strength are becoming prone to break. Therefore, the inducement of lower thermal expansion property to ceramic materials for higher heat resistant applications to reduce internal stress to be triggered by the rapid thermal shock is important. Ceramic materials in composition of the LAS ($Li_2O \cdot Al_2O_3 \cdot SiO_2$) family are generally spotlighted as materials for parts of structural ceramics despite disadvantages in respect of mechanical characteristics because the materials are regarded as having a potential to develop another heat resistant materials exploiting the inherent low thermal expansion properties thereof [3-7].

Ceramic compounds like eucryptite $(Li_2O \cdot Al_2O_3 \cdot 2SiO_2)$, spodumene $(Li_2O \cdot Al_2O_3 \cdot 4SiO_2)$, or petalite $(Li_2O \cdot Al_2O_3 \cdot 8SiO_2)$ are belong to ceramic materials of LAS family [8-10] and are generally synthesized through methods of sol-gel, or of colloidal mixing. In particular, the petalite to be heated up beyond the temperature of 1093 °C would reveal irreversible crystallographic transformation in the solid solution of β -spodumene and amorphous silica. The β -spodumene would show rather smaller values of strength, fracture toughness, and thermal conductivity comparing to other structural materials however, it shows an excellent thermal resistance owing to its lower thermal expansion property [11].

The pyrophyllite $(Al_2O_3 \cdot 4SiO_2 \cdot H_2O)$ is one of materials of aluminum silicate that shows low refractoriness owing to its high level of SiO₂ content with less ignition loss, less post firing shrinkage and better sinterability. These properties enable the pyrophyllite to be applied to raw materials to produce refractories¹¹ without going through the process of calcination to make Chamotte. The pyrophyllite available as domestic raw material to produce ceramic products is thus an eligible one owing to its composition for the synthesis of ceramics having low thermal expansion [12, 13].

In this study, the synthetic behavior of ceramics having low thermal expansion was examined to produce the petalite from pyrophyllite by adding Li_2CO_3 or $LiOH \cdot H_2O$, respectively. For purposes of this study, the lithium

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additives were mixed with the pyrophyllite in various mixing ratio and the synthesis and densification behavior as well as thermal expansion behavior were examined.

Experimental Procedure

Synthesis of petalite

For the synthesis of petalite, the pyrophyllite which is available in abundance in regions of Wando island area of Jeollanam-do province in Korea was used as a starting raw material of which details of chemical composition is summarized in Table 1. The average particle size of pyrophyllite powder used for the synthesis was distributed in the range of $1.0 \sim 5.0 \mu m$; and the weight ratio of main components of SiO₂ and Al₂O₃ was 8 : 2 that exhibited about 4% of ignition loss.

The weight ratio of petalite was calculated based on molar ratio of $Li_2O \cdot Al_2O_3 \cdot 8SiO_2$; and Li_2CO_3 or $LiOH \cdot H_2O$ were added respectively in place of Li_2O . The mixing ratios of Li_2CO_3 or $LiOH \cdot H_2O$ for synthesis of petalite powder are represented in Table 2.

Each component were milled and mixed for 24 h in the bottle made of polypropylene with isopropyl alcohol solvent and zirconia ball media. The mixtures were dried and then calcined at 800 °C for 1 h in an air atmosphere. The calcined powders were uni-axially pressured under 10 MPa and the powder compacts were sintered at 1100 °C ~ 1250 °C for 1 h with 4 °C/ min heating schedule.

Analysis of characteristics

To examine the characteristic of thermal decomposition behavior of the powder mixture, the thermal analyzer (STA 1500, Santon Redcroft, U.K.) was employed at each interval of temperature reached 1000 °C under the heating rate of 5 °C/min. The X-ray diffractometer (Rigaku D/MAX 2200, Japan) was also employed to examine the behavior of crystallization of specimen at each temperature. The analysis was done with CuK α

Table 2. Mixing ratios of Li_2CO_3 or $LiOH \cdot H_2O$ for Synthesis of Petalite powder.

Pyrophyllite (g)	Li ₂ CO ₃ (g)	LiOH • H ₂ O (g)	mixing ratio (wt%)
20	2	_	10:1
20	3	_	6.7:1
20	4	_	5:1
20	_	1	20:1
20	_	2	10:1
20	_	2.5	8:1

radiation (wavelength, $\lambda = 1.540$ Å), an operating voltage of 40 kV, scan step of 0.02 ° and a scan speed of 4 °/min. To observe the powder morphology and surface of sintered samples, the scanning electron microscope (SEM, Hitachi, S-3500N, Japan) was also used. The linear shrinkage of sintered specimen was measured with cylindrical pellet of the size of 10 mm (diameter) × 50 mm (length). The density was calculated by measuring the volume and weight of sintered specimen. The thermal expansion behavior of prepared sintered specimen were observed using the dilatometor (DIL 402 PC, Netzsch) at the range of room temperature to 1000 °C under the heating rate of 5 °C/min.

Results and Discussion

The thermal analysis behavior of powder mixtures are illustrated in Fig. 1 and 2. For the case of the mixture employing Li₂CO₃, the peaks of endothermic exothermic phenomena attributable to the and dehydration of absorbed water and oxidation reaction of organic substance were observed to the extent of 500 °C; and the endothermic reaction observed in the interval of 500 °C ~ 600 °C together with rapid weight reduction was estimated to be attributable to the decomposition of Li2CO3 and constituent H2O in pyrophyllite. The exothermic peak appeared in the interval of 750 °C ~ 800 °C was estimated to be attributable to the interaction of pyrophyllite with Li2O that synthesized the crystal of petalite. For the case of LiOH · H₂O, the endothermic reaction occurred with rapid weight reduction in the interval of 400 $^{\circ}$ C ~ 600 $^{\circ}$ C would be a phenomenon resulted from the decomposition of constituent H₂O of LiOH · H₂O and pyrophyllite. The wide exothermic peak observed at the temperature of 800 °C was estimated that it was resulted from the synthesis of crystal of



Fig. 1. DTA-TG curves of pyrophyllite : Li_2CO_3 mixture (mixing ratio = 6.7 : 1 wt%).

Table 1.	Composition	of Pyrophyllite	(wt%)
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SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	CaO	MgO	Na ₂ O	K ₂ O	S	Ig.loss	Total
4.19	19.86	0.19	0.52	-	_	-	0.10	0.05	5.09	100.00



Fig. 2. DTA-TG curves of pyrophyllite : LiOH \cdot H₂O mixture (mixing ratio = 20 : 1 wt%).



Fig. 3. XRD patterns of synthesized petalite prepared with various mixing ratio of Li_2CO_3 (heating temp. : 1250 °C)

petalite by the mutual reaction of pyrophyllite and Li_2O .

In the powder mixture samples heat-treated at 1000 °C, the petalite was synthesized together with the formation of lot of α -quartz phase. Thus the synthesizing temperature was increased to 1250 °C to examine the synthesizing behavior at each mixing ratio, and results obtained therefrom are represented in Fig. 3 and 4. In the case of Li₂CO₃, more developed β-spodumene peak was observed at the mixing ratio of 6.7:1 wt% that added the Li₂O more than the standard quantitative ratio of 8.6:1 wt% based on stoichiometric petalite composition. The reason of excessive amount of Li2CO3 was estimated that it could be attributable to the partial vaporization and resulted loss of Li constituent during the process of drying and heat treatment of the mixture. For cases of the mixing ratios of 5 : 1 wt% and 10 : 1 wt%, the minor phases of α quartz and lithium silicate (Li₂SiO₃) were observed besides the crystal phase of β-spodumene. In the case of LiOH \cdot H₂O, a change in relative ratio between β spodumene and α -quartz was observed. In all cases, the β spotumene crystal phase was observed with α -quartz crystal phase. In particular, the peak intensity was relatively decreased as the LiOH \cdot H₂O content increases.

Based on results of the synthesis at each mixing



Fig. 4. XRD patterns of synthesized petalite prepared with various mixing ratio of LiOH \cdot H₂O (heating temp. : 1250 °C).



Fig. 5. XRD patterns of heat-treated powder compacts prepared from 6.7 : 1 wt% ratio (pyrophyllite : Li₂CO₃) at various temperatures.

Table 3. Density and Shrinkage of Powder Compacts Prepared from 6.7:1 wt% Ratio (Pyrophyllite : Li₂CO₃) at Various Sintering Temperatures.

Temperature (°C)	Density (g/cm ³)	Shrinkage (%)
1100	2.16	16.3
1150	2.42	19.8
1200	2.41	19.9
1250	2.40	19.6

ratio, the green compacts of the powder of pyrophyllite and Li₂CO₃ mixed by the ratio of 6.7 : 1 wt% were prepared by pressure forming and then fired at 1100 °C, 1150 °C, 1200 °C, and 1250 °C for 1 h respectively. The crystallization behavior of the heat-treated samples is represented in Fig. 5. The β -spodumene phase was observed from all cases and the phases of α -quartz and lithium silicate were hardly observed at all temperatures due to the enhanced reactivity of the powder compacted by pressure. The glass phase was observed from the specimen fired at the temperature beyond about 1200 °C. And considering the case of pure petalite that would yield the formation of liquid phase at the temperature about 1350 °C in the phase diagram, the tiny amount of



Fig. 6. SEM micrographs of (a) pyrophyllite powder (b) synthesized petalite powder prepared from 6.7:1 wt% ratio (pyrophyllite : Li_2CO_3) (heating temp. : 1250 °C).



Fig. 7. SEM micrographs of sintered petalite at 1250 °C for 1 h (a) 6.7 : 1 wt% ratio (pyrophyllite : Li₂CO₃) (b) 20 : 1 wt% ratio (pyrophyllite : LiOH • H₂O).



Fig. 8. SEM micrographs of sintered petalite prepared from 6.7 : 1 wt% (pyrophyllite : Li_2CO_3) heated at (a) 1100 °C (b) 1150 °C (c) 1200 °C and (d) 1250 °C for 1 h.

low-melting-point phase formed from the reaction between pyrophyllite and Li_2O can be speculated owing to the excess amount of Li beyond the stoichiometry composition.

The changes of shrinkage and density of the compacts sintered at each temperature are represented in Table 3. The powder compacts revealed the shrinkage of about 20% at the temperature of 1200 °C with the density of 2.41 g/cm³ and the excessive glass phase was formed from the temperature of 1300 °C without significant changes in shrinkage and density.

The microstructures of the pyrophyillite used this study and the synthesized powder derived from 6.7:1 wt% mixing ratio of pyrophyllite to Li₂CO₃ are illustrated in Fig. 6. Contrary to the angulated shape of the pyrophyllite powder, the shape of synthesized powder revealed slightly increased granular growth and comparatively homogeneous grain size.

The microstructures of the powder compacts sintered at 1250 °C are represented in Fig. 7. In the sintered



Fig. 9. Thermal expansion behavior of synthesized petalite prepared from 6.7:1 wt% (pyrophyllite : Li₂CO₃).

sample employing Li₂CO₃, the rapid grain growth was observed by the formation of glass phase. On the contrary, no significant grain growth and densification were found in the case the LiOH · H₂O was added. It may be due to the few glass phase formation owing to the loss of Li and relative abundance of the crystal phase of α -quartz. The fracture surface of sintered compacts was also observed to examine the densification behavior of the specimen of 6.7:1 wt% of Li₂CO₃ along with varied temperatures, and the results are represented in Fig. 8. At the temperature of 1100 °C, the pores formed in the sintered body were observed. However, the compact rendered the densified microstructure from the sintering temperature of 1150 °C together with the grain growth by the liquid phase sintering. Based on results of the observation of microstructure of sintered compact and those summarized in Table 3, it was identified that the densification of compact was initiated from the temperature level around 1150 °C and continued further in the process synthesized to produce the petalite.

Fig. 9 represents the thermal expansion behavior of the synthesized petalite made from the powder to which the Li₂CO₃ was added and sintered at 1200 °C. The very low level of thermal expansion coefficient of $-0.43 \times 10^{-6/\circ}$ C was measured despite the presence of tiny amount of α -quartz and Li that forms liquid phase. And considering the thermal expansion coefficient of $5 \sim 6 \times 10^{-6/\circ}$ C of the pyrophyllite used therefor, the measurement reveals a notable reduction in thermal expansion coefficient of sintered compact and, this suggests the successful production of petalite ceramics of low thermal expansion. The increase of thermal expansion started from the temperature of 700 °C was not observed through the X-ray diffractometry, however it was estimated that it would be a phenomenon revealed by the phase transformation of the tiny amount of α -quartz to β -phase.

Conclusions

In this study, the petalite which is characterized by its

low thermal expansion was synthesized and the resulted characteristics were examined by employing the pyrophyllite available from local reserves.

In the synthesis of petalite, the β -spodumene which was the high temperature transition phase of petalite was observed from the synthesis of the pyrophyllite to which the Li₂CO₃ or LiOH \cdot H₂O was added respectively. In the synthesis conducted with the addition of Li₂CO₃, the case of the mixing ratio of 6.7 : 1 wt% (pyrophyllite : Li₂CO₃) rendered the petalite of less 2nd phase; and in the case of the synthesis added LiOH \cdot H₂O, the relatively abundant presence of α -quartz was resulted.

The petalite synthesized with Li₂CO₃ was almost densified by the liquid-phase sintering at the temperature of 1200 °C. The liquid-phase sintering was started from the temperature level of about 1150 °C and thereby the densification of sintering compact continued. And the thermal expansion coefficient of densified specimen appeared to be -0.43×10^{-6} /°C. Thus these results suggest that the locally available pyrophyllite could be effectively exploited to synthesize the petalite of negative thermal expansion of LAS family.

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