<u>Ceramic</u>

Processing Research

Characteristics and densification behavior of anorthite powder synthesized by a solution process employing a polymer carrier

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Crystalline anorthite (CaO·Al₂O₃·2SiO₂) powder was synthesized below 1000°C by a solution process employing a polymer carrier. Polyvinyl alcohol (PVA), having different molecular weights, was used as an organic carrier for preparation of the precursor ceramic gel. The PVA content, its degree of polymerization and type of silica sol had a significant influence on the specific surface area and morphology of the powder, and its crystallization behavior. The polymer content and its molecular length had an effect on the cation distribution in the solution and resulted in different crystallization behavior. Abnormally, omisteinbergite (CaO·Al₂O₃·2SiO₂), which has the same composition as anorthite, was observed prior to crystallization of anorthite. A more porous morphology and higher specific surface area were obtained with a higher content of the PVA polymer. The milled, amorphous-type anorthite powder was densified to a relative density of 94% below 1000°C.

Key words: Anorthite, Polyvinyl alcohol, Omisteinbergite, Crystallization, Densification.

Introduction

In 1967, Pechini patented a process which has been used to produce many kinds of oxide ceramic powders [1, 2, 3]. The process utilizes hydroxycarboxylic acids (i.e. citric and lactic acids) in combination with polyhydroxyl alcohols (such as ethylene glycol) to form a resin through condensation reactions. The acid acts as a chelating agent which chemically binds the cations that are dissolved in the solution. The polymerization is based on the polyesterification between the metalchelate complexes and polyhydroxyl alcohols. Due to the chelating action of the hydroxy carboxylic acids and the polymeric network, the cations have low mobility, so that precipitation is hindered. The result is ceramic powders with better chemical homogeneity and smaller particle size.

A rather simple-structured and inexpensive polymer, polyvinyl alcohol (PVA), can be used as the polymeric carrier [4-9]. Nitrate ions, as cation sources for oxide ceramic powders, become oxidizing agents for the decomposition of PVA. The PVA operates as a steric entrapment mechanism in the organic-inorganic solution, due to its large chain molecule. The properties of PVA depend on its degree of polymerization, degree of hydrolysis, and distribution of the hydrolyzed groups. The hydroxyl groups hinder the solubility due to strong hydrogen bonding between the intra- and intermolecular OH group. The intra and intermolecular bonding can be reduced if there are residual acetate groups which are hydrophilic. The PVA process also produces carbonaceous material that gives heat through its combustion, so that porous and single-phase powders can be formed from a homogeneous precursor solution at a relatively low external temperature [10].

Anorthite ceramics are candidates as ceramic substrates since anorthite has a low thermal expansion coefficient, low dielectric constant and high resistance to deformation by heat [11]. Nevertheless, anorthite ceramics have not been applied as a low-firing substrate due to the difficulty of sintering and crystallization below 1000°C. Kobayashi and Kato [12] investigated the low-temperature fabrication of anorthite ceramics using pure kaolin and calcite with fine particles at 1000°C. They obtained densified anorthite which had a relative density of 94%. Dense anorthite ceramics could be produced from sol-gel and glass-ceramics processes by firing around 1000°C [13]. However, the processes are very expensive and complicated.

In the present study, anorthite powder was synthesized by the PVA steric-entrapment route. The effects of the degree of polymerization and content of PVA, and type of silica sol on the crystallization behavior and powder characteristics of anorthite ceramic were studied. In addition, to find out the possibilities for applications of anorthite as low firing ceramic substrate materials, amorphous-type anorthite powder was ground and its effect on densification was examined.

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Experimental

Calcium nitrate, aluminum nitrate and silica sol were dissolved in stoichiometric proportions in deionized (DI) water. Two different colloidal silica types (Ludox AS40: 40% silica sol, pH of 9.1, surface area of 135 m²/g, and Ludox SK: 25% silica sol, pH of 4-7, surface area of 230 m²/g) were used. Once the cation sources were completely dissolved, the 5 wt% PVA polymer (78% hydrolyzed PVA) was dissolved in DI water and added to the solution. To examine the effect of degree of polymerization (DP) of PVA on the powder synthesis, two kinds of PVA was used. High-DP PVA has a DP value of 1625 (monomers/polymer), and low-DP PVA has a DP value of 428. The high DP PVA had a molecular weight of 153,000, and the low DP PVA had a molecular weight of 40,000.

The proportions of the PVA to cation sources in the solution were adjusted in such a way that there were 1, 2, 4, 6 or 8 times more positively charged valences from the cations than from the potentially negatively charged -(OH) functional groups of the polymers. The polymeric long chains have hydroxyl groups in solution. Hence, one PVA monomer, which has one hydroxyl (OH) functional group, can be used as a unit for calculation of the PVA content. The exact relative amount of PVA to cations in the solution can be calculated with reference to a monomeric unit of PVA.

Water was evaporated by continuous stirring during heating at 150°C on a hot plate. The resulting gel-type precursors were completely dried for several hours at 100°C. The dried, organic/inorganic precursors were then ground and were calcined or crystallized at various temperatures in an air atmosphere in a box furnace. Amorphous anorthite powder was planetary milled at 200 rpm for 20 h. The charge included 20 g powder with zirconia ball media having ball diameters of 5 mm. The jar volume was 250 ml and 100 ml iso-propyl alcohol was used for wet milling. The planetary milled and dried powder was uniaxially pressed at 20 MPa. The pellet-shaped, green compacts were sintered, and then characterized.

The development of crystallization was studied as a function of temperature using X-ray diffractometry (XRD, Dmax 2200, Rigaku/USA, Danvers, MA). The specific surface areas of the planetary milled powders were obtained by five-point BET analysis from nitrogen gas adsorption (Model ASAP 2400, Micromeritics, Norcross, GA, USA). Measurements of average particle size were conducted using an electrophoretic light scattering spectrophotometer (ESL-8000, Photal, Tokyo, Japan). The thermal expansion coefficient was determined by a recording dilatometer (Netzsch Dilatometer, 402 E, Germany) up to 1000°C at a heating rate of 5°C per minute. The dielectric constants were characterized with a HP4275 A impedance analyzer operated at room temperature at 1 MHz. The morphologies of the

Table 1. Crystallization behavior of anorthite precursors fired at $900^{\circ}C$ ~ $1000^{\circ}C$, according to type of silica sol and degree of polymerization of the PVA

Silica sol	Temperature (°C)				
source & PVA type	900	950	1000		
Ludox SK, PVA 205S	Amorphous	Omisteinbergite	Anorthite		
Ludox SK, PVA 540S	Omisteinbergite	Omisteinbergite	Omisteinbergite		
Ludox AS40, PVA 205S	Omisteinbergite	Omisteinbergite	Omisteinbergite & Anorthite		
Ludox AS40, PVA 540S	Omisteinbergite	Omisteinbergite	Omisteinbergite		

densified anothite were examined by scanning electron microscopy (SEM, Model S3500, Hitachi, Tokyo, Japan).

Results and Discussion

The DP of PVA had a significant influence on the homogeneity of the precursors and development of crystalline phase. The results of the crystallization behavior of the precursors derived from 4:1 ratio are listed in Table 1. All samples were fired at 900°C ~1000°C for 1h at a 4°C per minute heating rate. The development of the crystalline phase was dependant on the DP of the PVA polymer and silica source. In all cases, except for the precursor derived from Ludox SK and PVA 205S, the omisteinbergite phase (CaO·Al₂O₃· 2SiO₂) was observed at 900°C. The phase was still present up to 1000°C, while anorthite phase was observed in the precursor derived Ludox SK and low D.P. PVA. The molecular length of PVA can affect the distribution of cations in the solution [6-8]. In addition, the silica particle size in the silica sol can also affect the homogeneity and reactivity of the precursor. These phenomena resulted in a difference of crystallization behavior. In particular, it is abnormal that the omisteinbergite phase was produced prior to anorthite, in comparison with other chemical syntheses [12, 13].

The crystalline phases were also dependant on PVA

Table 2. Crystallization behavior of anorthite precursors fired at 900°C~1000°C, according to PVA content, in the case of employing high D.P. PVA and Ludox SK

PVA	Temperature (°C)				
content	900	950	1000		
1:1	Omisteinbergite	Omisteinbergite & Anorthite	Anorthite		
2:1	Omisteinbergite	Omisteinbergite & Anorthite	Anorthite		
4:1	Omisteinbergite	Omisteinbergite	Omisteinbergite		
6:1	Omisteinbergite	Omisteinbergite	Omisteinbergite		
8:1	Omisteinbergite	Omisteinbergite	Omisteinbergite		

Table 3. Crystallization behavior of anorthite precursors fired at 900°C~1000°C according to PVA content, in the case of employing low D.P. PVA and Ludox SK

DVA content	Temperature (°C)			
r vA content	900	950	1000	
1:1	Omisteinbergite	Omisteinbergite & Anorthite	Anorthite	
2:1	Omisteinbergite	Omisteinbergite & Anorthite	Anorthite	
4:1	Amorphous	Omisteinbergite	Anorthite	
6:1	Amorphous	Omisteinbergite	Anorthite	
8:1	Amorphous	Omisteinbergite	Anorthite	

content. The crystallization behavior according to PVA type and its content are summarized in Table 2 and Table 3. In the high DP PVA, the anorthite phase was observed in with the higher content of PVA of 1:1 and 2:1 ratio. By contrast, the anorthite phase was observed at 1000°C in all PVA contents for the low DP PVA. These results mean that the PVA content and its molecular length had a significant influence on the synthesis of anorthite. The effect of DP of the PVA may be attributed to the polymer length between cations in the solution. The low DP PVA had smaller polymer chain lengths than did the high DP PVA; therefore, it could make the range of distances between cations in the solution shorter. The different distance between cations according to PVA type may result in different synthesis mechanism involving combustion, oxidation and nuclear creation.

Figure 1 summarizes the BET specific surface areas of each powder fired at 900°C and 1000°C, with the low DP PVA. The specific surface area increased as the PVA content increases. This is attributed to higher content of PVA and, hence, more porous powder structure. At 1000°C, the specific surface area was less than the value at 900°C. This may be caused by full



Fig. 1. Variation of BET specific surface areas for fired powders as functions of temperature and PVA content, in the case of employing low D.P. PVA and Ludox SK.



Fig. 2. SEM micrographs for powder morphology at different PVA content of (a) 1:1 ratio and (b) 8:1 ratio, in the case of employing low D.P. PVA and Ludox SK.

crystallization and pre-sintering between particles.

Figure 2 illustrates the morphologies of the powders fired at 900°C, with the low DP PVA. The powder derived from the 1:1 ratio PVA content showed a more porous microstructure. The higher the content of PVA, the softer and more porous was the powder obtained. The organic-inorganic precursors derived from the PVA process resembled an aerogel and were formed by the development of foam during the stirring and solution drying process. The foam was generated during evolution of NO_x gases caused by the decomposition of the nitrates. The expansion of the gel due to the evolving NO_x gas continued until the precursors dried completely. The many kinds of evolved gases caused by the pyrolysis of PVA during the calcination resulted in the more open microstructure.

In this study, the anorthite precursor derived from Ludox SK and 4:1 ratio content of low DP PVA, which shows a complete anorthite phase below 1000°C, was chosen for the planetary milling process to examine the densification and crystallization behavior of milled powder. Porous and amorphous anorthite powder, as calcined at 900°C, was planetary milled. Table 4 lists the planetary milling effect on the amorphous powder. The specific surface area of the milled powder increased significantly in the first 1h milling time. The milling was conducted for 20 h, and finally the powder was ground to fine particles which had an average particle

Table 4.	Planetary	milling	effect	of	the	amorpl	10us-typ	e
anorthite p	owder deri	ved from	Ludox	SK	and	4:1 rati	o of PV	ΙA
(205S) con	tent							

	Specific surface area (m ² /g)	Average particle size (µm)
Before milling	5.2	irregular
Milling for 20h	22.0	0.3-0.4

Table 5. Development of crystalline phases of planetary milled, amorphous-type anorthite powder fired at 900°C~1000°C. The powder was derived from Ludox SK and 4:1 ratio of PVA (205S) content

Silica sol source	Temperature (°C)			
& PVA type	900	950	1000	
Ludox SK, PVA 205S	Amorphous & Omisteinbergite	Anorthite & Omisteinbergite	Anorthite	

size of 0.3-0.4 mm and specific surface area of 22 m^2/g .

The development of crystalline phases in the planetary milled powder is summarized in Table 5. The omisteinbergite phase was observed at 900°C and anorthite was detected with omisteinbergite at 950°C. The crystallization temperature moved down in comparison with the as-calcined powder. The lower crystallization temperature may be attributed to the un-stable amorphous powder, which contained significant internal stresses, caused by the powerful impact energy during the planetary milling. In particular, omisteinbergite was observed prior to crystallization of anorthite in this process. In other chemical syntheses, crystalline wollastonite (CaO·SiO₂) was normally observed prior to forming of the anorthite phase [14].

The densification behavior of the planetary milled, amorphous-type anorthite compacts is shown in Fig. 3. The compacts densified rapidly between 800~900°C which was accompanied by large shrinkage. Nearly 30% linear shrinkage occurred during the densification. The shrinkage almost stopped above 900°C, which was the temperature of formation of omisteinbergite. Final-



Fig. 3. Variation of relative density and linear shrinkage of planetary milled, amorphous powder compacts fired at 800°C, 900°C and 1000°C.



Fig. 4. SEM micrograph of anorthite sintered at 1000°C for 1h.

ly, a relative density of 94% was obtained below 1000°C. The reduction of the densification rate above 900°C may be due to the crystallization of omisteinbergite. In the densification behavior of the CaO-Al₂O₃-SiO₂ system, retardation of densification is caused by the rapid formation of crystalline wollastonite and phase separation prior to complete densification [15]. The poor densification was solved in this PVA process by the control of the crystalline phase and crystallization temperature. Formation of omisteinbergite above 900 °C did not disturb the densification at 800~900°C and the densification was successfully achieved by the planetary milled, un-stable amorphous powder which had a high surface energy. The microstructures of the densified anorthite are shown in Fig. 4. The anorthite sintered at 1000°C showed a relatively dense microstructure.

The variation of dielectric constant and thermal expansion coefficient of the polycrystalline anorthite, sintered at 900°C, 950°C and 1000°C are presented in Table 6. The dense anorthite sintered at 1000°C had a thermal expansion coefficient of $4.8 \times 10^{-6/9}$ C and a dielectric constant of 7.6. As shown in Table 5, omisteinbergite and the amorphous phases at 900°C and 950°C increased the thermal expansion coefficient and dielectric constant.

Conclusions

Anorthite-type powders prepared by the PVA steric entrapment route derived from Ludox SK silica sol and PVA with a low degree of polymerization were

Table 6. Dielectric constant (k) at 1 MHz and thermal expansion coefficient (a) of densified, polycrystalline anorthite sintered at 900°C, 950°C and 1000°C

	Temperature (°C)		
-	900	950	1000
κ (at 1MHz)	8.6	8.0	7.6
α (×10 ⁻⁶ /°C)	6.3	5.4	4.8

successfully crystallized and densified below 1000°C. The PVA content and its molecular length affected the crystallization behavior and powder morphology. The polymer content and its molecular length had an influence on the cation distribution in the solution, and resulted in crystalline development. In addition, the polymer contributed to a soft and porous powder microstructure, and planetary milling with the porous and amorphous-type powder was effective in making low firing anorthite ceramics. Stresses in the ground powder from the powerful planetary milling resulted in a decrease of the crystallization temperature, and it made it possible to obtain stable, anorthite phase below 1000°C. Moreover, the rapid densification in the amorphous and fine particles between 800°C~900°C was possible because of the formation of crystalline phases above 900°C. Finally, this new process is expected to enable the fabrication of low-firing anorthite ceramics.

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