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Characterization of Low Temperature Mullitization

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Abstract

Anomalously low temperature mullitization was observed in the precursor prepared by the Nishio and Fujiki's method using aluminum nitrate nonahydrate (ANN), aluminum iso-propoxide (AIP), and silicon ethoxide (TEOS) and its mechanism was examined by various methods. The low temperature mullitization was found to occur only when the precursor was once heat-treated at 250°C before heating up to crystallization. The heat-treated precursor showed two-step mullitization with small amounts of mullitization at 450°C and large amount of mullitization at 900°C. On the other hand, the as-prepared precursor showed one-step mullitization at around 900°C. The presence of two small regions with slightly different chemical composition was found in the particles of the heat-treated precursor samples by ^{29}Si nuclear magnetic resonance (NMR) spectra, small angle X-ray scattering (SAXS) and X-ray Rietveld analysis. The low temperature mullitization was considered to occur at the interfaces of the two small regions because they acted as the heterogeneous nucleation sites.

Introduction

Since mullite, $Al_{4+2x}Si_{2-2x}O_{10-x}$, is one of the important ceramic materials, mullitization from various starting materials has been intensively investigated by many workers.[1,2] Mullite precursors prepared by various methods are known to be grouped into two types of mullitization pathways. One type shows direct mullitization from the amorphous phase at around 1000°C whereas another one shows formation of the spinel phase at similar temperatures and mullitization occurring at higher temperatures. i.e. around 1200°C. The former precursor is considered to be in the homogeneous mixing state for SiO_2 and Al_2O_3 components, whilst the latter precursor is considered to be in an unhomogeneous state.[3] On the other hand, some workers recently reported the mullitization which could not be grouped into these two categories. Mullitization by these precursors occurred at much lower temperatures than those of the mullitization at around 1000°C. Huling and Messing[4] first reported such low temperature mullitization phenomena. They prepared precursors by drying a sol prepared from ANN and TEOS, followed by aging the gel in a steamed atmosphere at 80°C. The precursor crystallized directly to orthorhombic mullite at 700°C. Fischer *et al.*[5] reported similarly low temperature mullitization for the precursors prepared from aluminum sec-butylate and silicon chloride. Mullite formed by low temperature mullitization was extremely richer in the Al_2O_3 composition (88 mol%) than the ordinary composition (60 mol%) and its lattice showed $a > b$ relation; the opposite to those of the ordinary mullites. Nishio and Fujiki[6] prepared mullite long fibers using the sol–gel method. They found that mullite started to crystallize at 600°C from the amorphous state when it was heated, as fibers formed though mullitization occurred at around 1000°C when the powdered sample was heated. We have categorized this as low temperature mullitization in this paper because the mullitization occurred below 900°C.

A different feature was suggested in low temperature mullitization compared with those of the ordinary mullitizations which occur at around 1000°C and/or above 1000°C. However, the mechanisms of low temperature mullitization has not been extensively investigated. The purpose of this study is, therefore, to prepare a precursor which shows low temperature mullitization and to characterize the low temperature mullitization process.

Experimental Procedure

The preparation of precursors used in this study was based on the method reported by Nishio and Fujiki.[6] In this preparation, ANN was first dissolved in deionized water and AIP and TEOS were added to this solution in that order. The aqueous solution was stirred for 2 days at room temperature, and then gelled and dried at 110°C for 36 h. This xerogel was designated as the as-prepared sample. A part of the as-prepared xerogel was heat-treated at 250°C for 16 h and was referred as the heat-treated sample. In order to compare the mullitization behavior of these samples, two other samples were prepared the following way. The starting solution was prepared by dissolving ANN in ethanol and then by adding TEOS. It was stirred at room temperature for 3 h. Then, a homogeneous type precursor was prepared by slowly hydrolyzing TEOS and gelling the solution by water included in ANN at 60°C for 4 weeks. An unhomogeneous type precursor was prepared by adding ammonia into the solution which formed a precipitation. The homogeneous and unhomogeneous type precursors were designated as the slowly hydrolyzed (SH) method sample and the rapidly hydrolyzed (RH) method sample, respectively. Chemical composition of all these samples was arranged to Al_2O_3 = 60 mol%, i.e. $3Al_2O_3{\cdot}2SiO_2$ composition.

High resolution solid state magic angle spinning nuclear magnetic resonance (MAS-NMR) spectra were obtained at 70·26 MHz for ^{27}Al and 53·4 MHz for ^{29}Si using a JEOL GX-270 system. The samples were contained in the zirconia rotor. The ^{29}Si spectra were obtained using a pulse width of 2 μs and a recycle delay of 60 s. The ^{27}Al spectra were obtained using a pulse width of 1 μs and a recycle delay of 10 s. The spinning frequency for the both spectra was 3·8 kHz. The chemical shift (δ) of ^{29}Si spectra was referenced by tetramethylsilane at δ = 0·0 ppm, in which the chemical shift was referenced by polydimethylsilane at δ = −33·8 ppm. The chemical shift of ^{27}Al spectra was referenced by $Al_2(SO_4)_3{\cdot}18H_2O$ at δ = 0 ppm.

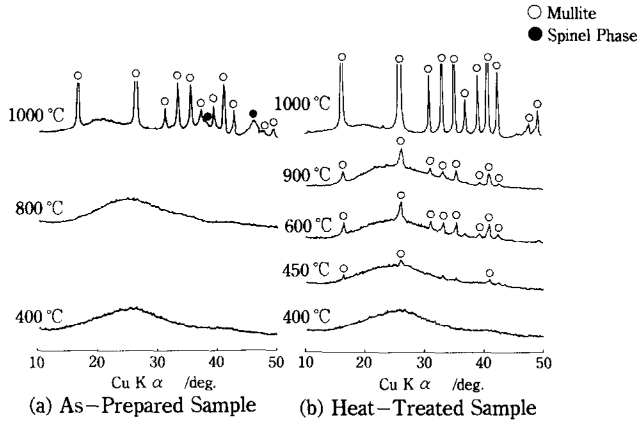
Infrared absorption (IR) spectra were obtained by the KBr disk method using a JEOL JIR-6000 system. A pellet was prepared by mixing 0·01 g of sample with 0·25 g of KBr powder and formed by a uniaxial press. The spectra were measured for a wave number range between 400 and 4000 cm^{-1}. Differential thermal analysis (DTA) curves were measured from room temperature to 1100°C at a heating rate of 10°C/min using about 20 mg of sample. Small angle X-ray scattering (SAXS) measurements were carried out using a glass cell 10 mm in width. The range measured was between 0·1 and 3·0 nm^{-1} in a scattering vector using Mo Kα radiation.

Each sample was fired at 400–1000°C for 1 h and the crystalline phase in their samples were examined by powder X-ray diffraction (XRD) using Cu Kα radiation monochromated by a graphite. The XRD measurements were performed by two scanning methods. Measurements for identification of the crystalline phase were made by the usual continuous scanning method with a scanning speed of 1°/min for a scanning range from 10–50° in 2θ. Structural parameters for some mullites were refined by the Rietveld method[7] using the RIETAN program.[8] The XRD profiles for the Rietveld analysis were measured using the step scanning method with a step scanning width of 0·02° and a fixed time of 20 s for a scanning range from 30 to 100° in 2θ. The details of the structure refinement procedure was reported elsewhere.[9] The amount of mullite formed was evaluated from the scale factor obtained by the Rietveld analysis.

Results and Discussion

Figure 1 shows the XRD patterns of the as-prepared samples and the heat-treated samples heated at various temperatures. The as-prepared sample heated at 400–800°C showed an amorphous pattern. Mullite and a small amount of spinel phase were observed in the as-prepared sample heated at 1000°C. In contrast, mullite began to crystallize at 450°C in the heat-treated sample.

Mullite formation curves in the as-prepared sample, the heat-treated sample, the SH method



(a) As−Prepared Sample (b) Heat−Treated Sample

Fig. 1. XRD patterns of the as-prepared sample (a) and the heat-treated sample (b) fired at various temperatures for 1 h.

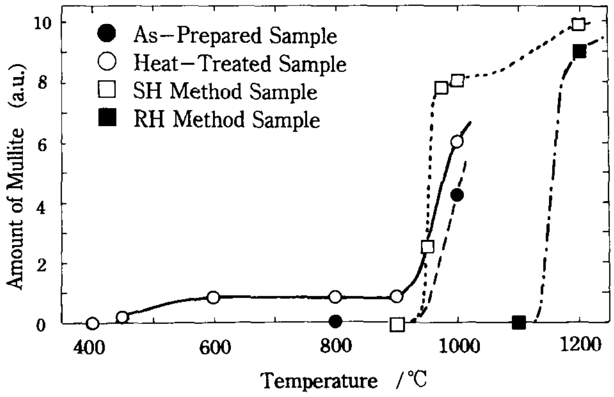
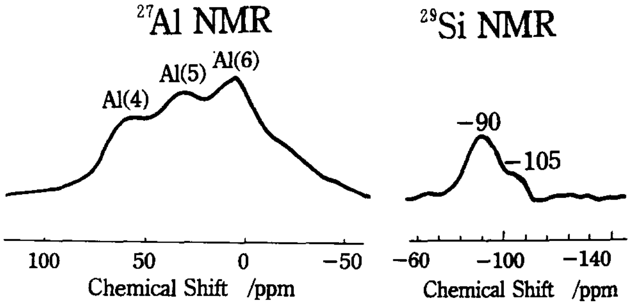


Fig. 2. Formation curves of mullite in the as-prepared sample (●), the heat-treated sample (○), the SH method sample (□) and the RH method sample (■).

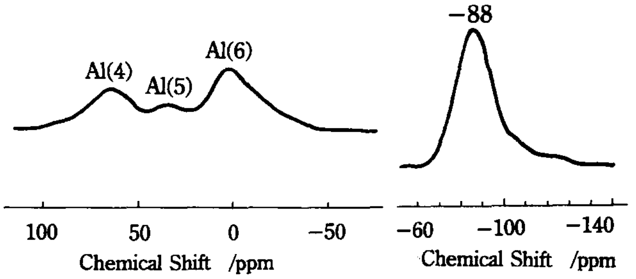
sample and the RH method sample are shown in Fig. 2. In the as-prepared sample and the SH method sample, mullite started to crystallize from around 900°C and the amount increased very rapidly by 950°C, especially in the SH method sample. Mullitization in the as-prepared sample was similar to that in the SH method sample. The lower mullite formation content of the as-prepared sample can be interpreted by the co-presence of spinel phase in this sample. In the RH method sample, mullite started to crystallize from around 1100°C and the amount increased very rapidly to around 1200°C. The higher mullitization temperature of this sample was attributed to the formation of the spinel phase at around 1000°C before mullitization. On the other hand, mullite started to crystallize from around 450°C in the heat-treated sample. The amount of formed mullite was, however, very small and did not increase up to 900°C. The amount of mullite rapidly increased from 900°C, and no spinel phase formation was observed at 1000°C as shown in Fig. 1. The mullite formation curve of the heat-treated sample was largely different with respect to the starting temperature of mullitization but was similar with respect to the temperature in which most of the sample crystallized to mullite, i.e. the temperature was at around 1000°C and was similar to those of the as-prepared sample and the SH method sample.

In order to examine the influence of the heating time for the low temperature mullitization, the heat-treated sample was heated at 800°C for 24 h but there was no significant increase in the amount of mullite formed.

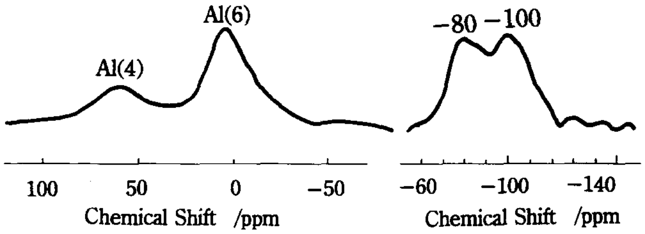
Chemical composition of the mullites formed at 600, 800 and 900°C was analyzed by the X-ray Rietveld method. We also evaluated the chemical composition of the mullites from the length of *a*-axis. The chemical compositions of the mullites obtained from both methods were around 66 mol% Al_2O_3. The XRD of these mullites showed the similar pattern with those of the tetragonal-like mullite[10] but did not show the XRD pattern of orthorhombic mullite as reported by Huling and Messing[4] and also the relation of $a > b$ as reported by Fischer *et al.*[5]



(a) Heat−Treated Sample



(b) SH Method Sample

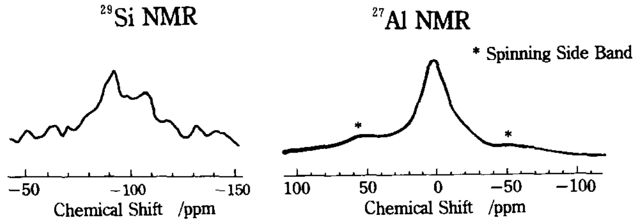


(c) RH Method Sample

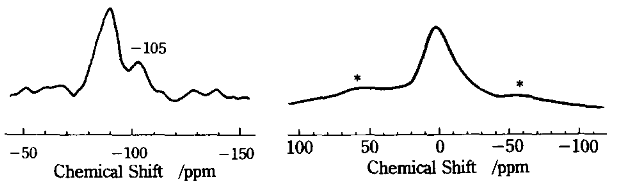
Fig. 3. ^{29}Si and ^{27}Al NMR spectra of the heat-treated sample (a), the SH method sample (b) and the RH method sample (c). All samples were calcined at 600°C for 1 h.

Figure 3 shows ^{29}Si and ^{27}Al NMR spectra of the heat-treated sample, the SH method sample, and the RH method sample. All the samples were calcined at 600°C for 1 h. The ^{27}Al NMR spectra showed a complex profile and two or three peaks overlapped. Peaks were observed at around 5, 40 and 60 ppm and were assigned to six-, five- and four-coordinated Al atoms, respectively.[11] The intensity of the five-coordinated Al peak showed a trend to decrease as the mullitization temperature of the samples increased and no five-coordinated Al peak was observed in the RH method sample. The ^{29}Si NMR spectra showed one or two peaks depending upon the samples. The spectrum of the SH method sample showed only a single peak at around −88 ppm. This peak may be assigned to $Q^4(2Al)$ or $Q^4(3Al)$,[11] i.e. corresponding to the Q^2 or Q^1 state for the SiO_4 tetrahedral structure. On the other hand, two peaks at around −80 and −100 ppm were observed in the spectrum of the RH method sample. They may be assigned to the Q^0 and Q^3 or Q^4 structures, respectively. The spectrum of the heat-treated sample also showed two peaks and they were observed at around −90 and −105 ppm. Therefore, they may be assigned to the Q^1 or Q^2 and Q^3 or Q^4 structures, respectively.

The following models are proposed for the structure of precursors from the results of ^{27}Al and ^{29}Si NMR spectra. The precursor of the SH method sample has a homogeneous structural state and SiO_2 and Al_2O_3 components are considered to be uniformly mixed at the molecular level. On the other hand, the precursor of the RH method sample consisted of two different structural regions

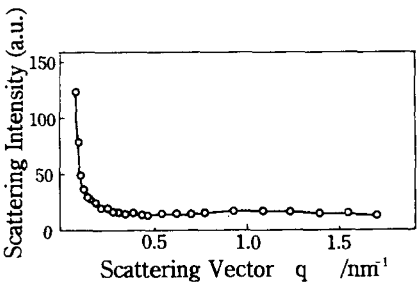


(a) As-Prepared Sample

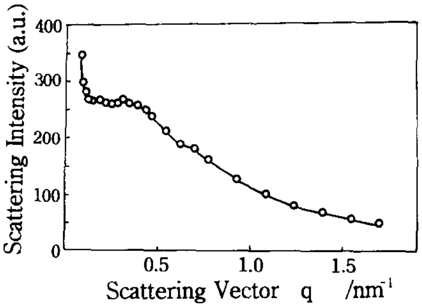


(b) Heat-Treated Sample

Fig. 4. ^{29}Si and ^{27}Al NMR spectra of the as-prepared sample (a) and the heat-treated sample (b).



(a) As-Prepared Sample



(b) Heat-Treated Sample

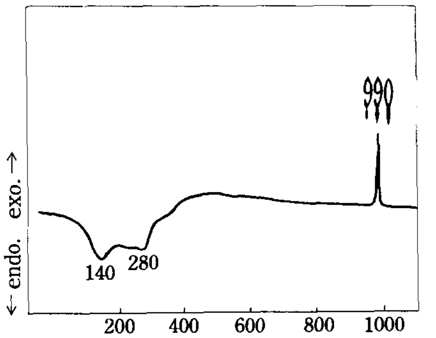
Fig. 5. SAXS curves of the as-prepared sample (a) and the heat-treated sample (b).

which may correspond to an Al-rich and Si-rich chemical composition. Such a separation of chemical composition in the precursor is the reason for the phase change into the spinel phase and amorphous silica at around 1000°C before mullitization.[1] The precursor of the heat-treated sample may also consist of two different composition regions with a slightly Al-rich and Al-poor composition from the starting bulk composition.

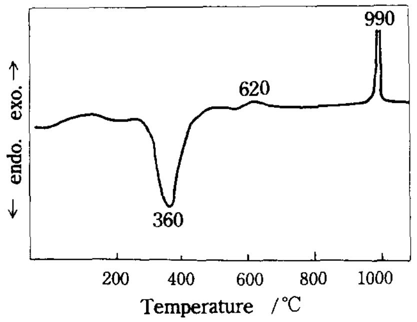
In order to elucidate further details of the heat-treated sample, ^{29}Si and ^{27}Al NMR spectra of the heat-treated and the as-prepared samples are compared and are shown in Fig. 4. In the ^{27}Al NMR spectra of both samples, little difference was observed except for some broadening of the six-coordinated Al peak in the heat-treated sample. However, there was a certain difference between their ^{29}Si NMR spectra. The spectrum of the as-prepared sample showed broad complex peaks ranging from -80 to -120 ppm, therefore, they were considered to consist of a number of overlapped peaks. This indicates that there were various polymerization states in SiO_4 tetrahedra of this sample. On the other hand, the spectrum of the heat-treated sample showed two clear peaks at -90 and -105 ppm. These peaks can be assigned to Q^1 or Q^2 and Q^3 or Q^4 structures, respectively. It may indicate that there were two different states in the polymerization structure of SiO_4 tetrahedra of the heat-treated sample. Since this sample shows low temperature mullitization, whereas the as-prepared sample shows no low temperature mullitization, the difference of these polymerization states of SiO_4 tetrahedra is suggested to correspond to the difference of mullitization in the both samples.

Figure 5 shows SAXS curves of the as-prepared sample and the heat-treated sample. In the as-prepared sample, SAXS was observed only in the small scattering vector ($\mathbf{q}$) range of $\mathbf{q} < 0{\cdot}2\ \mathrm{nm}^{-1}$. It is attributed to scattering from considerably larger scattering species corresponding to the sub-micron size region, in which size corresponds to the particle size of the precursor samples. On the other hand, the SAXS curve of the heat-treated sample showed not only the scattering in the range of $\mathbf{q} < 0{\cdot}2\ \mathrm{nm}^{-1}$ but also the broad scattering in the range of $\mathbf{q} > 0{\cdot}2\ \mathrm{nm}^{-1}$. This broad scattering is attributed to the scattering from relatively smaller scattering species corresponding from angstrom to nanometer order size region. From these SAXS data, we can conclude that the heat-treatment of the sample at 250°C caused very small unhomogeneous structure regions in nanometer size within the precursor particles.

The DTA curves of the as-prepared sample and the heat-treated sample are shown in Fig. 6. Some difference was observed between the two DTA curves. In the DTA curve of the as-prepared sample, endothermic reaction was observed in a wide temperature range from 100 to 400°C. They consisted of some numbers of overlapped endothermic peaks, which were caused due to the various reactions such as dehydration, dehydroxylation and the decomposition of nitrate and alkoxyl groups. On the other hand, the DTA curve of the heat-treated sample differed largely from that of the as-prepared sample and showed a clear single endothermic peak at 360°C. During the heat-treatment at 250°C, a partial thermal decomposition of the hydroxyl groups and the rearrangement of the precursor structure are suggested to occur in the sample. In the DTA curve of the heat-treated sample, a weak and broad exothermic peak was



(a) As-Prepared Sample



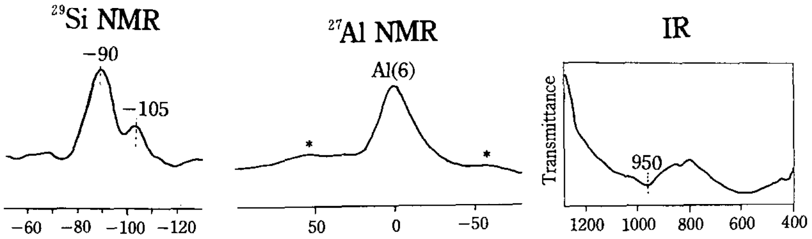
(b) Heat-Treated Sample

Fig. 6. DTA curves of the as-prepared sample (a) and the heat-treated sample (b).

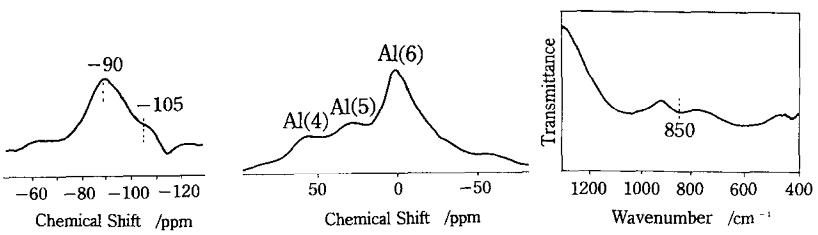
detected at around 620°C but was not observed in that of the as-prepared sample. This exothermic peak may be corresponding to the low temperature mullitization. On the other hand, the exothermic peak at 990°C was attributed to the crystallization of mullite. Although the intensity of the exothermic peaks in these samples showed little difference, it can be interpreted by the difference of weight loss of the samples with and without heat-treatment at 250°C.

As mentioned in Fig. 1, mullite started to crystallize at 450°C in the heat-treated sample. Therefore, the endothermic peak at 360°C is considered to be important for low temperature mullitization. To examine the structural change by this endothermic reaction, the heat-treated sample was further heated at 400°C for 1 h. The IR and NMR spectra of the heat-treated sample and the sample further heated at 400°C are shown in Fig. 7. The ^{27}Al NMR spectrum of the heat-treated sample showed only a single peak at 0 ppm, which is assigned to six-coordinated Al structure. On the other hand, the ^{27}Al NMR spectrum of the sample heated at 400°C showed three peaks at 0, 30, and 60 ppm, which are assigned to six-, five-, and four-coordinated Al structures, respectively. Evolution of the four- and five-coordinated Al structures were found in the sample heated at 400°C and this structural change was considered to be derived from the dehydration of Al–OH. On the other hand, changes in the ^{29}Si NMR spectra was not observed except for a little broadening of the peaks and the two peaks still remained at –90 and –105 ppm in both samples. The broadening of the peaks may be related to the condensation reaction of Si–OH and Al–OH by dehydration. In the IR spectrum of the heat-treated sample, a weak absorption band was observed at 950 cm^{-1}, in which the absorption band resembles that of the OH group in diaspore (α–AlOOH).[12] In the IR spectrum of the sample heated at 400°C the absorption band was not observed, whereas a weak and broad absorption band at 850 cm^{-1} was observed. Since the absorption band at 850 cm^{-1} may be assigned to that of the condensed AlO_4 tetrahedra,[12] it is also a comparable result to explain the condensation reaction of Al polyhedra by heating at 400°C.

We found that heat-treatment at 250°C was very important in causing low temperature mullitization. Structural change during this treatment was characterized by various methods and the following change was observed: dehydration and



(a) Heat-Treated Sample



(b) Sample fired the Heat-Treated Sample at 400°C

Fig. 7. IR and ^{29}Si and ^{27}Al NMR spectra of the heat-treated sample (a) and the sample further heated the heat-treated sample at 400°C (b).

decomposition of part of the nitrate and alkoxyl groups occurred due to the treatment. This change introduced very small unhomogeneous structural regions with a slightly different chemical composition in the precursor particles. These two regions remained even after heating at 400°C, by which temperature condensation and re-arrangement of the precursor were considered. When such small regions with different chemical compositions are present within the particles, the interfaces between them are considered to be energetically active and can act as the heterogeneous nucleation sites. Therefore, low temperature mullitization can occur in the interfaces only by heating at relatively low temperatures. The amount of mullite formed by low temperature mullitization was, however, small because the mullitization occurred only in the interfaces of two regions in the precursor particles. The experimental result was that no apparent increase in the formation amount of mullite occurred, even though the duration at the low mullitization temperature is compatible with the consideration mentioned above.

Conclusions

Mullite precursor was prepared from the combination of ANN, AIP and TEOS based on the Nishio and Fujiki's method[6] and the mullitization process was examined using various methods. The following conclusions were obtained:

(1) Heat-treatment at 250°C was essentially necessary for the low temperature mullitization and the heat-treated precursor started to show mullitization at 450°C.
(2) The formation curve of mullite in low temperature mullitization showed a two-step curve with small amount of mullitization at 450°C and large amount of mullitization at 900°C.
(3) The precursor to show the low temperature mullitization had two small regions with slightly different chemical composition within the precursor particles.
(4) The interfaces between these two regions in the precursor particles played an important role as the heterogeneous nucleation sites for low temperature mullitization.

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