Journal of the European Ceramic Society 16 (1996) 149–153
© 1996 Elsevier Science Limited
Printed in Great Britain. All rights reserved
0955-2219/96/$15.00
0955-2219(95)00170-0

Effect of Aging Temperature on the Structure of Mullite Precursor Prepared from Tetraethoxysilane and Aluminum Nitrate in Ethanol Solution

Kiyoshi Okada,* Chikako Aoki,† Takayuki Ban, Shigeo Hayashi & Atsuo Yasumori
Department of Inorganic Materials, Tokyo Institute of Technology, O-okayama, Meguro, Tokyo 152, Japan

Abstract

The effect of aging temperature on the structure of mullite precursor prepared by dissolving tetraethoxysilane (TEOS) and aluminum nitrate nonahydrate (ANN) in ethanol was investigated by liquid state ^{29}Si and ^{27}Al nuclear magnetic resonance (NMR) spectroscopy, small angle X-ray scattering (SAXS), powder X-ray diffraction (XRD) and solubility of ANN in ethanol. The aging temperatures examined were from 25 to 60°C. With increasing aging temperature, polymerization of TEOS progressed, size of sol particles increased, and solubility of ANN largely increased but little change occurred in the coordination state of the Al ion. Mullite was obtained as the main crystalline phase only when the precursor solution aged at 60°C was fired at 1000°C, whereas the spinel phase was obtained as the main crystalline phase instead of mullite from the solutions aged at the other temperatures. It was therefore concluded that silica and alumina components in the precursor solution were in an intimately mixed state when the precursor solution was aged at 60°C, but those aged under 60°C were not as intimately mixed as the former. Intimate mixing of both components was achieved in the precursor solution aged at 60°C by trapping of ANN solution in silica gel network.

1 Introduction

Mullite has been actively investigated by many workers during the last decade[1] and its good mechanical properties, especially at high temperature, are recognized. It is, therefore, expected to be a candidate material for high temperature applications under an oxidizing atmosphere. Various kinds of starting materials and preparation methods were studied as the raw materials for mullite ceramics.[1] Generally, their starting materials are in an amorphous state and mullitization occurs at high temperature before the densification. Although a variety of results on this subject were reported, mullitization pathways can be divided into two types on the whole as reviewed by Okada *et al.*[2] One type shows direct mullitization from an amorphous state and the other type shows a spinel phase[3] formation before mullitization. The former type occurs in the starting materials with a good mixture of silica and alumina components, whereas the latter occurs in starting materials with a poor mixture of silica and alumina components. These two types have been widely accepted by many workers. In Ref. 4, however, we found that the crystalline phase of the thin film fired at 1000°C and prepared by dip-coating the solution by dissolving TEOS and ANN in ethanol varied from mullite to spinel phase by changing the aging time of the same solution at room temperature. In order to elucidate this phenomenon the structural state of the mullite precursor in the solution and the effects of the aging time at room temperature were investigated by liquid state ^{29}Si and ^{27}Al NMR, SAXS and XRD techniques.[5] The following results were obtained: polymerization of TEOS progressed very quickly and most of the Si atoms formed Q^3 and Q^4 structures within a very short reaction time. Here, the superscript figures in Q represent the number of Si–O–Si bonds per one Si atom. On the other hand, Al atoms showed a monomer state and formed an octahedral structure and it did not change throughout the experimented aging time. It was, therefore, found that the precursor did not form an aluminosilicate complex and silica and alumina components were not so homogeneously mixed in the solution.

In this paper, we investigate the effect of aging

---

*To whom correspondence should be addressed.
†Now with Japanese Patent Office, 3-4-3 Kasumigaseki, Chiyoda, Tokyo 100, Japan.

temperature on the structure of mullite precursor prepared by dissolving TEOS and ANN in ethanol to further elucidate this subject.

2 Experimental Procedure

Precursor solution with $3Al_2O_32SiO_2$ composition was prepared by dissolving 0·24 mol/l of TEOS and 0·72 mol/l of ANN in ethanol. Since ANN contains $9H_2O$ per one Al atom, the H_2O/TEOS is 27 and this amount of water is highly excessive for polymerization of TEOS. The precursor solution was aged at various temperatures in a sealed plastic bottle up to 100 days. The aging temperatures experimented were 25, 40, 50 and 60°C.

Liquid state NMR measurements were performed by JEOL JNM-GSX500 equipment. The spectra of ^{29}Si NMR were recorded at 99·361 MHz using a pulse width of 14·9 μs and a delay time of 1 s. The spectrum was obtained by accumulating 6000 times because the spectrum signal was very weak. A teflon tube instead of a glass tube was used for the measurements to avoid the signal from a glass tube. Chromium acetylacetonate and tetraethoxysilane were added to the solution just before the measurements were made and mixed. The former reagent was used to reduce the spin-lattice relaxation time and the latter one was used as an internal chemical shift standard. The spectra of ^{27}Al NMR were recorded at 130·315 MHz using a pulse width of 1·5 μs and a delay time of 1 s. The spectra were obtained only by accumulating 240 times because the spectrum signal was strong enough in this case. A silica glass tube was used for the measurements. ANN solution was used as an external chemical shift standard.

SAXS measurements were performed by Rigaku RINT-1500 equipment using Ni-filtered Cu Kα radiation (50 kV and 300 mA) through an evacuated beam path. The sample solution was mounted in a glass capillary 3 mm in diameter and 8 μm in thickness. Intensity measurements were made in the scattering angle 2θ from 0·13 to 3·49° with a step interval of 0·02° and a fixed time of 10 s. Since the obtained intensity (Io) didn't show a linear relation for log (Io) versus S^2 (S: scattering vector), the radius of gyration was calculated using the Fankuchen methods.[6] This value was further recalculated to particle size by assuming sphere shape.[6] The detection limit of particle size by the present experimental conditions was estimated to be up to around 100 nm.

XRD measurements were performed by Rigaku Geigerflex diffractometer using graphite monochromated Cu Kα radiation (40 kV and 20 mA). The samples for the XRD were prepared by inserting the precursor solution (2 ml) in an alumina crucible to a furnace kept at 500°C for 15 min to instantly dry and burn out any nitrate and alcohol, and then fired at 1000°C for 6 h.

Solubility of ANN in ethanol at each temperature was measured by a conventional method.

3 Results

3.1 Liquid state ^{29}Si and ^{27}Al NMR

Figure 1 shows ^{29}Si NMR spectra of the precursor solutions aged for 5 days at various temperatures. The spectrum of the solution aged at 25°C showed three peaks at around −91, −100 and −107 ppm. They are assigned to Q^2, Q^3 and Q^4 structures,[7] respectively. With increasing aging temperature, the peaks became weak and broad. The spectrum of the sample aged at 60°C showed no apparent peak and only a halo was observed due to the background signal by the teflon tube. Such a change in the spectra can be related to the hydrolysis and polymerization of TEOS to form a three-dimensional silica framework structure. The lack of peaks in the NMR spectrum can be explained by the formation of sol particles, in which structural information can not be detected by the liquid state NMR technique.

All the ^{29}Al NMR spectra of the precursor solutions aged for 5 days showed very sharp peaks at around 0 ppm. No significant differences were found among these spectra. These peaks are same as that of ANN used as an external standard. Therefore, Al atoms are considered to be in a monomer state with a regular octahedral structure. The spectra showed no change even with the

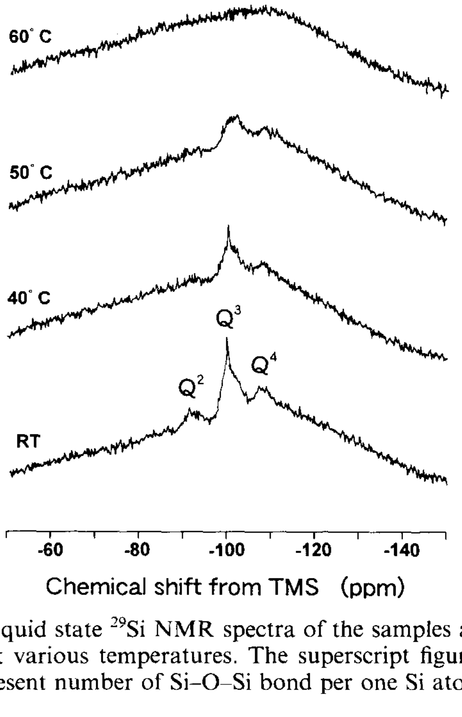

Fig. 1. Liquid state ^{29}Si NMR spectra of the samples aged for 5 days at various temperatures. The superscript figures in Q represent number of Si–O–Si bond per one Si atom.

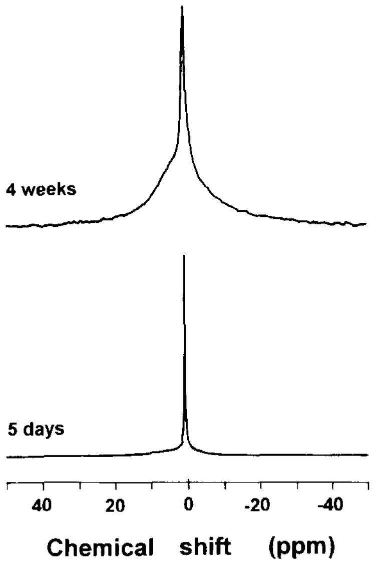

Fig. 2. Liquid state ^{27}Al NMR spectra of the samples aged at 60°C for 5 days and 4 weeks.

longer aging time when they were aged at 40 and 50°C just as in the case of room temperature aging reported before.[5] On the other hand, a certain change was observed in the spectra when they were aged at 60°C for a long time. The spectra aged at 60°C for 5 days and 28 days are shown in Fig. 2. The full width at half maximum (FWHM) of the peak at around 0 ppm apparently increased and a shoulder also appeared at around several ppm. The increase of FWHM can be attributed to the distortion of octahedra and the shoulder can be assigned to the polymerization of Al-octahedra such as dimer and/or oligomer from a monomer.

3.2 Sol particle size by SAXS

The size of sol particles was measured for the three samples, i.e. aged for 5 days at 25, 50 and 60°C. No clear indication of small angle X-ray scattering was observed for the sample aged at 25°C except for that from the instrument. It was, therefore, unclear whether sol particles were already formed in this solution or not. Even if the sol particles were present in the sample, they were smaller than several nm in size because this was a detection limit of the present experimental conditions. The other two samples showed small angle X-ray scattering corresponding to sol particles. The size of the sol particles was not uniform and had a distribution. By the Fankuchen method,[6] they were approximated by two particle size distributions for the both samples. Their particle sizes in the sample aged at 50°C were 7 and 14 nm whereas those at 60°C were 9 and 26 nm. Increase of the larger particle size was clear between these two samples and it may correspond to coalescence of small sol particles.

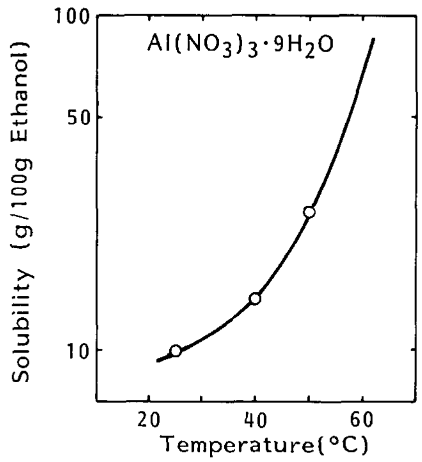

Fig. 3. Solubility curve of aluminum nitrate nonahydrate in ethanol as a function of temperature.

3.3 Solubility of ANN in ethanol

Figure 3 shows the solubility curve of ANN in ethanol. The solubility of ANN at 25°C is around 10 g in 100 g ethanol and is not very high. The solubility increased to 26 g at 50°C. We, however, could not accurately determine the solubility limit of ANN at 60°C because the solution became viscous and evolution of NOx gas was observed due to the decomposition of nitrate ion.

3.4 Crystalline phase at 1000°C

Intensities for the strongest reflection of mullite, which has fully overlapped peaks of 120 and 210 reflections and 400 reflection of spinel phase were qualitatively measured for the samples fired at 1000°C for 6 h. Their results are shown in Fig. 4. The sample aged at 25°C showed very weak reflections of mullite and spinel phase. Amount of crystalline phases was found to be low compared with the other samples. The samples aged at 40 and 50°C showed relatively intense spinel phase reflections but very weak mullite reflections. On the other hand, only the sample aged at 60°C showed

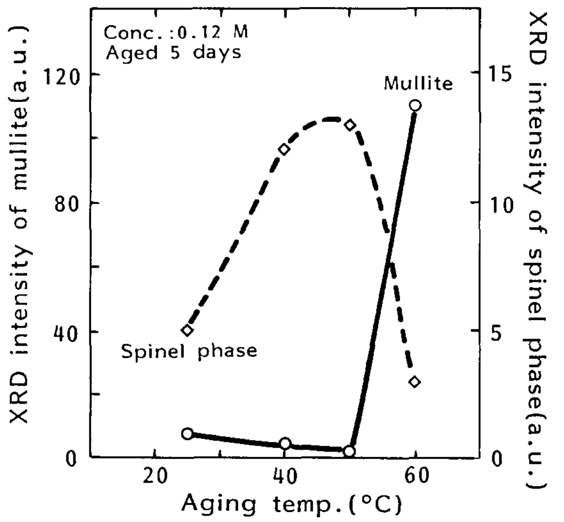

Fig. 4. XRD intensity of crystalline phases in the samples fired at 1000°C for 6 h aged at various temperatures.

strong mullite reflections with only a trace of spinel phase reflections. Thus, the crystalline phases formed by firing the precursor solutions at 1000°C were found to largely differ by the aging temperatures of the samples. Mullite formation was found to be only dominant in the sample aged at 60°C.

The crystalline phase in the samples aged for various times at various temperatures was also examined to clarify the effect of aging time. No dominant mullitization was found in all the samples aged for various times under 60°C. In the samples aged at 60°C, intensity of the mullite reflection of the 1 day aged sample was small. However, the mullite intensity increased with longer aging time and remained constant by aging over 5 days.

4 Discussion

Liquid state NMR data showed that polymerization of TEOS largely progressed but no change occurred in the monomer octahedral coordination of Al atoms with increasing aging temperature. No aluminosilicate complex was detected in the sol solution of the present preparation system. The presence of silica sol particles was also confirmed from the SAXS data. It was, therefore, concluded that the precursor was not in the molecularly mixed state in the solution, though direct mullitization occurred in the samples aged at 60°C. The precursors which show direct mullitization at around 1000°C have been considered to be in a very good mixing state and the silica and alumina components are molecularly mixed.[8] This may be generally true but it has been found from our results that it is not always necessarily true.

We observed a clear difference in the mullitization pathways between the precursors aged at 60°C and those aged under 60°C. What is the most important point to cause such a difference? Since the precursor did not form an aluminosilicate complex, both components need to be mixed to yield mullite directly. Two things are considered to be important for this. First, it is necessary for polymerized silica to be in small particles and it should form a gel network structure with them. Since the present solution is a very strong acid and contains a high concentration of salt in the present precursor system, the present experimental conditions are considered to be applicable to develop a gel structure rather than particles which is obtained using basic conditions.[9] The present SAXS data are compatible with this model. Second, the particles of the alumina component, which are considered to be nitrate, are also required to be small and present around silica gel. As mentioned before, the solubility of ANN in ethanol largely increased with increasing aging temperature. This means that ANN can be dissolved in ethanol up to a very high concentration when they are prepared at higher aging temperature. It is suitable to form a gel structure with a trapped solution of dissolved ANN in the silica gel network structure. The mixed state in silica and alumina is thought to be formed in this way in the sample aged at 60°C and these samples show direct mullitization as a result as has been shown by others previously.[10,11]

The present and previously reported results,[4] show that the crystalline phases are found to change not only by the aging conditions of the precursor but also by the firing conditions. The main crystalline phase by firing at 1000°C is mullite in the dip-coated thin films[4] from the solution aged at room temperature for short time, but it is the spinel phase in the present experiments. In this case the amount of precursor solution for firing is considered to be important and a cause of this difference. A very small amount of precursor was fired in the dip-coating[4] and was considered to be preferable for mullitization because of the rapid evaporation of the solvent. Recently, Nishio *et al.*[12] reported that the crystallization behaviour of mullite precursor prepared by the solution method changes due to the firing conditions such as the heating rate. We (Ref. 13) also found this and reported similar behavior recently. It is considered that heat treatment under several hundreds °C plays an important role on various reactions such as dehydration and decomposition of nitrates and alkoxyl groups which causes rearrangement of the precursor structure.

5 Conclusions

(1) With increasing aging temperature, polymerization of TEOS to form silica sol progressed.
(2) No apparent change was observed for a monomer octahedral structure of Al atoms irrespective of the aging temperature in a short aging time.
(3) Solubility of ANN in ethanol increased with increasing aging temperature.
(4) The main crystalline phase obtained by firing at 1000°C is mullite when the precursor solution was aged at 60°C, whereas it is the spinel phase when they were aged under 60°C.
(5) The mullite precursor in the present system was found not to form aluminosilicate com-

plex and silica and alumina components were not in a molecularly mixed state in the solution. Aging at 60°C was, however, suitable to prepare a well mixed state in silica and alumina components and yielded direct mullitization at 1000°C.

Acknowledgements

We thank Professor I. Ando and Dr. H. Kurosu of Tokyo Institute of Technology for use of the NMR instrument and various fruitful suggestions for the NMR measurements. A part of this study is financially supported by the 1991 Corning Research Grant.

References

1. Schneider, H., Okada, K. & Pask, J. A., *Mullite and Mullite Ceramics*. John Wiley & Sons, London, 1994.
2. Okada, K., Otsuka, N. & Somiya, S., Review of mullite synthesis routes in Japan. *Am. Ceram. Soc. Bull.*, **70** (1991) 1633–9.
3. Brindley, G. W. & Nakahira, M., The kaolinite–mullite reaction series: III. The high-temperature phases. *J. Am. Ceram. Soc.*, **42** (1959) 319–24.
4. Okada, K. & Otsuka, N., Preparation of transparent mullite films by dip-coating method. In *Ceramic Transactions, Vol.6, Mullite and Mullite Matrix Composites*, eds S. Somiya, R. F. Davis & J. A. Pask. Am. Ceram. Soc., Westerville, OH, 1990, pp. 425–34.
5. Aoki, C., Ban, T., Hayashi, S. & Okada, K., Characterization of polymeric structure of aluminosilicate complex in sol–gel solution. In *Third Euro-Ceramics*, eds P. Duran & J. F. Fernandez. Faenza Editrice Iberica S.L., Madrid, 1993, Vol. 1, pp. 387–92.
6. Nitta, I., *X-ray Crystallography (II)*. Maruzen, Tokyo, 1961, pp. 555–6.
7. Pouxviel, J. C., Boilot, J. S., Beloeil, J. C. & Zallemand, J. J., NMR study of the sol/gel polymerization. *J. Non-Cryst. Solids*, **89** (1987) 345–60.
8. Aksay, I. A., Dabbs, D. M. & Sarikaya, M., Mullite for structural, electronic, and optical applications. *J. Am. Ceram. Soc.*, **74** (1991) 2343–58.
9. Iler, R. K., *The Chemistry of Silica*, John Wiley & Sons, London, 1979, p. 174–6.
10. Hoffman, D., Roy, R. & Komarneni, S., Diphasic xerogels, a new class of materials: phases in the Al_2O_3–SiO_2 system. *J. Am. Ceram. Soc.*, **67** (1984) 468–71.
11. Komarneni, S., Roy, R., Fyfe, C. A., Kennedy, G. T. & Strokl, H., Solid-state ^{27}Al and ^{29}Si magic-angle spinning NMR of aluminosilicate gels. *J. Am. Ceram. Soc.*, **69** (1986) C42–4.
12. Nishio, T., Kijima, K., Kajiwara, K. & Fujiki, Y., The influence of preparation procedure in the mullite preparation by solution method to the mixing of Al and Si and the crystallization behavior. *J. Ceram. Soc. Jpn*, **102** (1994) 462–70.
13. Ban, T., Hayashi, S., Yasumori, A. & Okada, K., Low temperature mullitization. *J. Eur. Ceram. Soc.*, submitted.