

Clay Structural Transformations during Firing

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Keywords: Kaolinite, mullite, structural transformation

Abstract. Silicate ceramics with clays are some of the most complicated ceramic systems because of the very complex relationship between the behavior of mineral materials during the ceramic processing and the transformations during heating. A major challenge is to predict the phase transformations in silicate ceramics, since complex relationships occur between the microstructural and structural characteristics of fired product and the physical properties.

Clay minerals undergo strong structural transformations during heating, simultaneously to a complex path of thermal transformations. Individual reactions cannot simply be identified since they are closely related and overlapped. At temperature above 800°C, new phases are recrystallized and many of the reactions are strongly topotactic.

Mullite is the most important phase, which recrystallizes with a range of morphology and stoichiometry. Variables affecting the mullite formation include the clay mineral type and behavior during heating, the possible occurrence of liquid and impurities as Fe. It results in large variations of the stoichiometry and shape of mullite crystals, which are embedded in a low ordered phase to form a micro-composite microstructure.

This presentation will review recent research, looking at structural transformations in some typically used phyllosilicate systems : (i) structural transformation of kaolinite and mica phases were identified at temperature up to 1100°C. They evidence a residual structural order of high temperature phases which is favorable to the topotactic recrystallization of mullite; (ii) from the high temperature form of phyllosilicates, an organized network of mullite can be obtained; (iii) the composition of a local and transient liquid and the presence of minor elements as Fe has a significant influence on the mullite morphology; (iv) mechanical properties are closely related to size and organization degree of the mullite network; (v) the process itself influences the kinetic of structural transformation and particularly the powder compact density and the thermal cycle. These researches in silicate ceramics evidence multiple and complex challenges, providing opportunities for future development.

Keywords: Kaolin; Mullite (d); Sintering (a); X-ray methods (b)

Introduction

Kaolin is representative raw materials often used in the manufacture of ceramics. Kaolin are complex mixtures of more or less ordered kaolinite, a mica group mineral and quartz, and minor minerals can be present.

Mullite crystallization is the most frequent phenomenon involved in the structural transformation of clay minerals. The quantity and development of this phase influence the sintering mechanisms, but mullite formation depends on the raw material type and is modified by the firing process^[1 2 3 4]. In this paper, we present mullite crystallization from a kaolin raw material containing kaolinite as the major mineral and muscovite and quartz as minor minerals. We observed the thermal transformations in the absence of a liquid phase, i.e. at the early stage of mullite nucleation and growth, since the eutectic temperature of the hypothetically homogeneous material is at 1140°C^[5]. Mullite formation and characteristics

were studied in relation to temperature at 1100°C and 1150°C, and we used a 3°C/min and 20°C/min of temperature rates.

Material and methods

The kaolin (Bio, from Echassière, France) ^[6] has a mineralogical composition as 79±2% kaolinite, 17±2% muscovite mica and 4±1% quartz. The crystallinity degree of the kaolinite phase ^[7] is high (Hinckley index 0.98), compared to that of the well known kaolinite reference mineral Kga1 ^[8] (Hinckley index 1.03). For the muscovite mineral, the peak heights and broadening of the (001) X-ray reflections are very similar to those of a typical and well crystallised muscovite. Iron is distributed in muscovite structure and in Fe hydroxide.

X-ray diffractometry was carried out using a Debye-Scherrer system equipped with a curved position sensitive detector (CPS 120 Inel). The Cu K α_1 X-ray line was selected using a bent quartz crystal monochromator. All measurements were performed in a reflection mode and the incident angle of the beam onto the sample surface was fixed at 5°. This value allows the observation of diffraction lines in the low angular range, but increases the instrumental broadening effect. The direct observation of crystallite sizes was performed by transmission electron microscopy with a 200kV Jeol 2010. A drop of powder suspension was deposited onto an amorphous carbon film on a copper grid.

Results

X-ray pattern in Fig. 1a is from Bio fired at 1100°C, 3°C/min. The only crystalline phases are residual quartz, and the newly formed mullite. The micro-structural characteristics of the studied sample were determined by line profile analysis of the diffraction peaks and the instrumental line profile contribution was evaluated using the NIST standard sample LaB₆. For mullite, the diffraction integral breadths are much wider than those from the instrumental resolution function. This indicates an intrinsic broadening effect from the studied material. Breadth variations are much greater than the measurement uncertainties, which are about 0.01°2 θ .

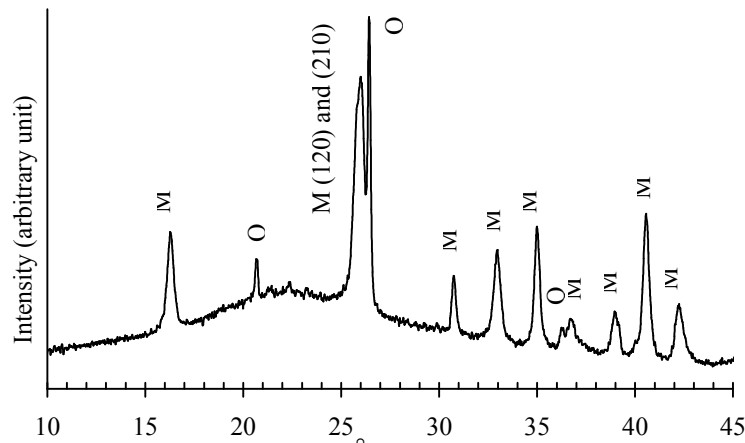


Fig. 1 : (a) : X-ray diffraction pattern of Bio kaolin sintered at 1100°C, 3°C/min.

The separation of the size and micro-strain effects was carried out using Williamson-Hall plots ⁹.

$$(\beta_{\text{obs}} - \beta_{\text{inst}})\cos \theta = \lambda/D_v + 4 \varepsilon_{\text{str}}(\sin \theta) \quad (1)$$

Where ε_{str} is the weighted average strain, β the integral breadth of a reflection (in radians 2 θ), located at 2 θ and D_v the volume weighted crystallite size. A typical result is presented in Fig. 2 for the sample fired at 1100°C, 3°C/min. For the two perpendicular directions, (hh0) and (00l), the plotted line slopes are very low, indicating that the main broadening effect is the

size effect. The anisotropy of the broadening effect is clearly shown. β values of the (hh0) diffraction lines are two or three time larger than that of the (00l) peaks. In Fig. 2, the non-zero intercept effect of the β line for the (hh0) reflection is close to 0.052 nm^{-1} and the corresponding value for the (00l) reflection is 0.022 nm^{-1} .

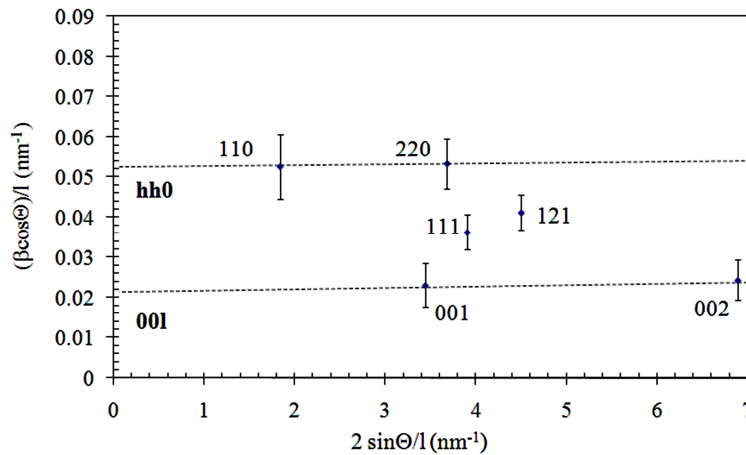


Fig. 2 : Williamson and Hall plot of (hh0) and (00l) directions of mullite, for samples preliminary sintered at 1100°C , $3^{\circ}\text{C}/\text{min}$.

The crystallite sizes reported in Table I, in relation to temperature and the temperature rate, show that mullite nano-crystals are always elongated along the c axis. The variations between values are significant when compared with measurement uncertainties.

Temperature rate	$3^{\circ}\text{C}/\text{min}$		$20^{\circ}\text{C}/\text{min}$	
	(00l)	(hh0)	(00l)	(hh0)
Temperature($^{\circ}\text{C}$)	L (nm)	L (nm)	L (nm)	L (nm)
1100	26 ± 4	16 ± 2	50 ± 10	21 ± 3
1150	48 ± 10	19 ± 3	50 ± 10	30 ± 3

Table I : Crystallite sizes of mullite from Bio kaolin, preliminary sintered at 1100°C , $3^{\circ}\text{C}/\text{min}$ and 1150°C . $20^{\circ}\text{C}/\text{min}$.

Images from transmission electron microscopy of Bio fired at 1100°C , $3^{\circ}\text{C}/\text{min}$ and 1150°C , $20^{\circ}\text{C}/\text{min}$ are presented in Fig. 3a and Fig. 3b respectively. The presence of an amorphous phase containing small needle like crystallites was observed. The crystalline phase was always identified as mullite by micro-diffraction although there were various crystallographic orientations.

Additional observations by local microanalysis of potassium and iron elements indicated the following: - Potassium is not present in mullite crystals or nearby. This strongly suggests that the amorphous phase results only from metakaolinite transformation, and not from the mica material produced by the high temperature; - Iron-rich small zones were detected in the amorphous phase, but did not relate to the position of mullite crystals.

The lattice parameters of mullite were calculated from the peak positions using an usual least square fit procedure. The precise positioning of the sample was calculated using the peak position of an internal standard (silicon NIST, SRM 640a) mixed with the studied sample. Results of a , b and c parameters and the lattice volumes are given in Table II against temperature and sintering rate.

		a (Å)	b (Å)	c (Å)	Vol (Å ³)
3°C/min	1100°C	7,5537	7,6976	2,8858	167,79
	1150°C	7,5560	7,6937	2,8859	167,76
20°C/min	1100°C	7,5681	7,7022	2,8858	168,21
	1150°C	7,5664	7,7017	2,8871	168,24
3°C/min	1100°C, 12h	7,5641	7,7013	2,8883	168,25
20°C/min		7,5626	7,7003	2,8877	168,16

Table II : Lattice constants of mullite from Bio kaolin preliminary sintered at 1100°C and 1150°C for two temperature rates; 3°C/min and 20°C/min. The 3rd and 4th lines are from materials sintered at 1100°C, 3°C/min and 20°C/min and maintained during 12 h.

Discussion

At the early stage of mullite crystallization, without detectable liquid phase, the crystallite sizes along (00l) and (hk0) directions vary with thermal treatment (Table I). All sizes increase as the temperature rises for both temperature rates. At a fixed temperature, however, the rise in the temperature leads to an increase in crystallite sizes. At 1150°C this increase is more accentuated. In particular at a temperature of 1150°C and at 20°C/min the anisotropic character of mullite crystallites decreases. A comparison with TEM observations (Fig. 3a and 3b) confirms the variation of the appearance relationship, although crystallite sizes are not representative.

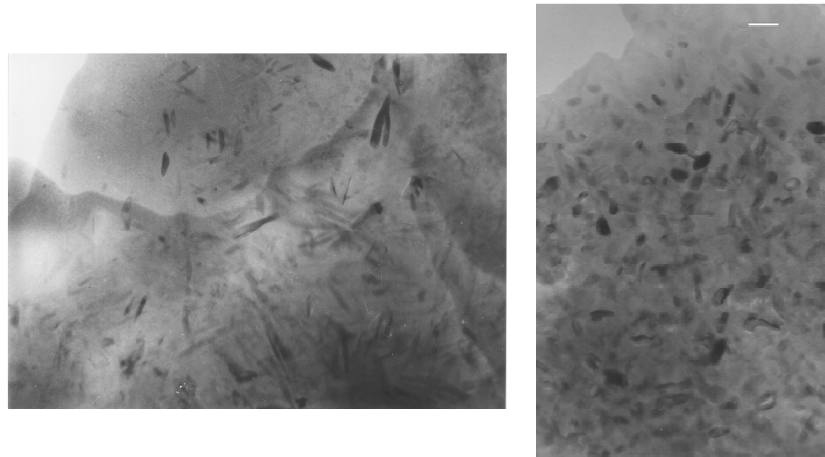


Fig. 3 : (a) : TEM image of mullite crystals in an amorphous material from Bio kaolin sintered at 1100°C, 3°C/min; (b) : Bio sintered at 1150°C, 20°C/min. Bar = 100 nm.

A connection between mullite quantity and mullite crystallite sizes can be made using previous results [7] with the same kaolin material. These showed that, at the 1100°C intermediate temperature, mullite quantity increased from 4.2 to 10 weight % when the sintering rate rose from 3 to 20°C/min. From sizes indicated in table 2, therefore, which vary sharply, it is suggested that the increase of the temperature to 1100°C has more effect on crystallite size rather than the crystallite number, i.e. the mullite growth mechanism.

Additional X-ray microanalysis indicated no correlation between potassium analyses and the mullite or the matrix phase. This shows that mullite needles are only found in the kaolinite-transformed phase. Consequently, the muscovite high temperature transformed phase behaves independently of neighboring phases, up to 1150°C.

Iron was analyzed only in very small rich zones located in the amorphous phase matrix. Its presence is not surprising since a small part of iron in Bio is initially found as a structural element of the kaolinite mineral. During heating, the important phase change in clay minerals leads to the formation of small clusters, mostly containing iron, which may be hematite [10].

Their distribution in the material has no correlation with that of mullite, which suggests that the role of iron in the mullite formation mechanism is very limited.

A linear correlation between the a mullite lattice parameter and the alumina content was found by Cameron^[11], especially for orthorhombic mullite. A more recent study from Okada^[12] proposed a slightly different linear relation for both pseudo tetragonal and orthorhombic structures. The discrepancy between the two interpretations is more noticeable at high alumina content and is caused by a relative variation in the a and c axis for the pseudo tetragonal phase caused by some lattice disordering. The resulting length for the c axis for pseudo tetragonal mullite is smaller than that for orthorhombic mullite, in the case of two mullites having the same a axis.

In this study, the mullite alumina content was calculated on the basis of Cameron (Fig. 4a-4b) linear relation, against the a lattice constant. The results were in a narrow range, about 62 to 65 Al₂O₃ %. Using the Okada correlation only slightly extended the alumina content to higher percentages. The standard deviation of Al₂O₃ content varies within the whole composition domain and is at about 1% for the range analyzed^[11, 12]. A significant difference, therefore, was found between samples obtained at 3°C/min and 20°C/min, but not influenced by temperature. The corresponding b distances for all samples are also plotted in Fig. 4a. They are close to values published by Cameron and Okada. Since a lengths differ sharply from b lengths, this should be a preliminary indication of the orthorhombic character of mullite. Additional information is provided by c length values (Fig. 4b), which fit the Cameron relation satisfactorily. The relatively short c lengths further support the fact that orthorhombic mullite is always found in Bio, at 1100 and 1150°C. It must be emphasized that lattice parameters are always situated inside the orthorhombic mullite area presented by Okada for a large number of various mullite, (figure 3 in¹²).

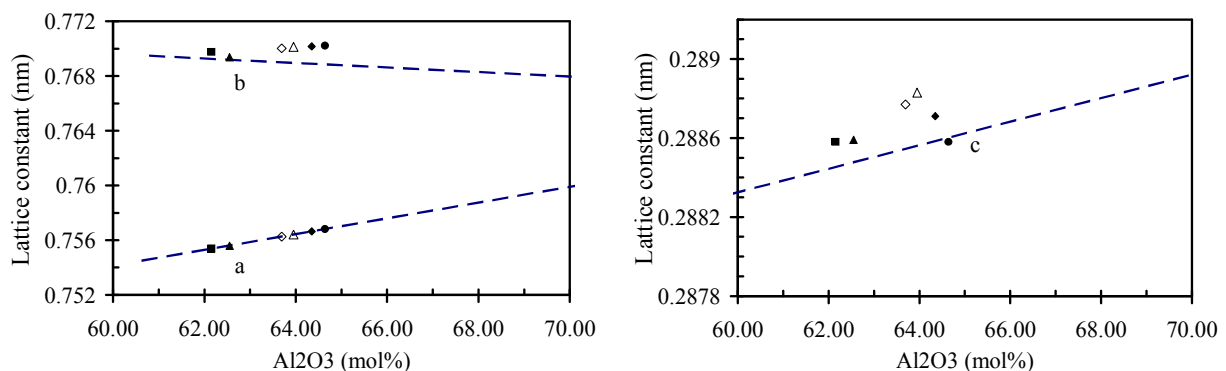


Fig. 4 : Lattice constants and cell volumes of mullite versus the thermal cycle, compared to the average data from¹². (a): a and b constants; (b) : c constant. (■): 1100°C, 3°C/min; (▲): 1150°C, 3°C/min; (●): 1100°C, 20°C/min; (◆): 1150°C, 20°C/min; (△) :1100°C, 3°C/min, 12h; (◇) : 1100°C, 3°C/min, 12h.

Table II shows a comparison made with samples, which were first sintered at both temperatures and temperature rates, but maintained at these temperatures for 12 hours. Results for a, b and c lattice parameters are given in Table 3 and plotted in Fig. 4. The c length appears to be slightly reduced, compared with the almost similar c lengths from materials sintered at 20°C/min. The very small variation from the above-mentioned results, compared with the measurement uncertainties, is not a precise indication of the stoichiometry variation and the modification of the orthorhombic character. Nevertheless, the clear splitting of the (120) and the (210) X-ray reflection lines of mullite supports this idea. In which case, there is no doubt that the very long sintering time encourages the presence of larger mullite crystals, reducing the X-ray line breadth. For samples sintered without any hold time, the apparent

reflection overlap is mainly due to the very low crystallite size. The presence of an orthorhombic mullite should not therefore be dismissed.

A transition from pseudo tetragonal to orthorhombic mullite was reported in [12, 13], i.e., at about 1200°C and 62 - 63 Al₂O₃ %, for various sintered mullites. For the sintered Bio material, it was observed that orthorhombic mullite occurs with alumina content up to about 65 % and at the 1100°C temperature.

In general, for kaolinite mineral, the formation routes of mullite are either a direct formation route or a transitory spinel phase formation before mullitisation, depending on the kaolinite phase and the thermal process [14, 15]. At the lowest temperatures, poorly ordered nano-crystals nucleate from the disordered metakaolinite phase. They correspond to pseudo tetragonal mullite. At a higher temperature, the process is governed by the growth of more ordered mullite crystals. Their stoichiometry is different because the growth stage implies a long-range diffusion between alumina-rich and silica-rich zones, which are segregated under the influence of temperature and time. This explains the stoichiometry difference between low and rapid thermal cycles of Bio, because the former one encourages silica enrichment. The presence of well-crystallized orthorhombic crystals in Bio indicates that mullite at the 1100°C temperature and above, for a 3 and 20°C/min temperature rate, is mainly transformed through a growth process. A similar trend is observed when comparing the cell volumes of rapidly sintered samples, which are almost equivalent, to cell volumes for 12 hour sintered samples.

Conclusion

Mullite formation from kaolinite was observed at the early stage of crystallization in the absence of liquid phase. Size and shape of crystals as the corresponding cell constants vary in relation to sintering temperature, but mainly in respect of the temperature rate. Using the Cameron relationship, it appears that mullite stoichiometry remains in a narrow composition domain. At high temperatures rates, in particular, the mullite silicon content is reduced. At the very least, orthorhombic mullite was identified, in spite of a relatively low temperature between 1100 - 1150°C.

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