

Thermal conductivity and specific heat of kaolinite: Evolution with thermal treatment

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Abstract

The structure and microstructure of a standard reference kaolin clay change significantly with thermal treatment. The consequences in terms of thermal conductivity and specific heat have been studied. Thermal conductivity measurements were made, using the laser flash technique, on the green body and samples subjected to thermal treatments at different temperatures between 700 and 1400 °C. The results show that the green body and kaolin treated at temperatures below 1050 °C exhibit low values of effective thermal conductivity, less than 0.3 W m⁻¹ K⁻¹. Higher temperature treatment yields a strong increase in thermal conductivity up to 3 W m⁻¹ K⁻¹. Through complementary characterization based on X-ray diffraction and scanning electron microscopy, this evolution as well as that of the specific heat is interpreted in terms of structural reorganisation of the clay, microstructural changes and crystallisation of mullite and cristobalite.

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1. Introduction

Clays are basic raw materials for the ceramic industry used in the manufacture of tiles, fireclay refractories and whitewares. Typically, the fabrication process involves a forming step where the raw material mixture is worked into the required shape, for example by pressing, and then a firing step to obtain a dense robust object. During firing both structural and microstructural changes take place in the clay material. The original clay is a hydrated aluminium silicate with a layered crystal structure in the form of fine grains. This transforms into an amorphous phase or a mixture of amorphous phase and crystallised phases (mullite and cristobalite) depending on the thermal treatment. Elimination of porosity will also take place. The topic of the present paper concerns thermophysical characteristics of clay before, during and after firing. These constitute vital information for the evaluation of energy consumption in manufacture, firing process optimisation and control of the final properties.

As early as 1887, Le Chatelier studied the thermal reactions occurring in clays on heating.¹ Then work by Simpson, Knote, Cohn and MacGee reported measurements of the heat involved in clay transformations and also that related to the specific heat.^{2–5} The values cited for specific heat in these early papers correspond to an average value measured for a large change in temperature (20–1050 °C). By 1929, dehydroxylation at approximately 500 °C and structural reorganisation at approximately 900 °C in clays had been identified, even if the exact origins of these phenomena were not yet well understood. Nowadays the improvement in characterization techniques such as electron microscopy, X-ray diffraction or calorimetry gives more precise knowledge of the microstructure of clays before and after a thermal treatment. The nature of raw materials (crystallography, mineralogy, size and shape of grains, etc.) can be determined as well as the influence of the firing cycle conditions or the presence of impurities, for example iron, on the microstructure of fired clays.^{6,7} As a consequence studies have been made to understand how different source clays lead to variation in properties such as shrinkage, frost resistance, water absorption or mechanical strength.^{8–11}

In contrast detailed knowledge of the thermal properties of clays, namely specific heat and thermal conductivity, is

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not complete. The specific heat of different source clays has been measured at low temperature, that is between 20 K and 600 K, and before any thermal treatment. The values, at room temperature, vary from 780 to 950 J kg⁻¹ K⁻¹.^{12,13} According to handbook data, the specific heat of kaolinite is 945 J kg⁻¹ K⁻¹ and this value increases to 1006 J kg⁻¹ K⁻¹ after dehydroxylation.¹⁴ Literature data on specific heat of pure clay materials subjected to higher temperature thermal treatment seems to be lacking. With respect to the thermal conductivity of clay-based materials, studies have mostly been limited to industrial products such as tiles, bricks and refractories fired at 900 °C and above. Using a guarded plate method Norton obtained values for refractory kaolin bricks at 400 °C ranging from 0.6 to 2.2 W m⁻¹ K⁻¹.¹⁵ The solid phase of a fired clay building brick, that is without porosity, exhibits a thermal conductivity between 0.8 and 1.1 W m⁻¹ K⁻¹ at room temperature.¹⁶ However, the overall or effective thermal conductivity of a clay material will be sensitive to factors such as size and volume fraction of pores, humidity, mineralogical composition including impurities, and thermal history. For example, Dondi et al. have investigated the influence of these factors in a statistical study of 29 clay bricks but, given the complexity of the problem, found it difficult to establish which ones were dominant for the thermal conductivity.¹⁷

Therefore the aim of this study was to relate the evolution of a standard reference kaolin clay in terms of: structural reorganisation, microstructural changes and finally crystallisation of mullite and cristobalite, to changes in the specific heat and the thermal conductivity.

2. Experimental procedure

A pure kaolin from Georgia, USA (with reference kga-1b), containing 96% of kaolinite, was selected for the study. It was sieved using a mesh of 100 μm and pressed in a die at 30 MPa to obtain cylindrical samples with dimensions of 2 mm in thickness and 13 mm in diameter. Samples were then thermally treated (heating rate: 5 °C/min) at 700, 1050, 1250, 1300, 1350 or 1400 °C for 1 h. The samples were characterized using X-ray diffraction (XRD) and scanning electron microscopy (SEM). Chemical etching with hydrofluoric acid was used to remove the amorphous phase before the microscopy observations. The transformations in the clay due to thermal treatment were also studied using differential thermal analysis. The pore volume fraction was evaluated by measurement of the sample density using the method based on Archimedes' principle.

The specific heat was measured, between 350 and 1150 °C, with a Setaram Multi-HTC calorimeter using a heat flux differential scanning calorimetry (HF-DSC) detector. The thermal diffusivity was measured with the flash technique using a neodymium-glass laser operating at 1.053 μm as the flash source to heat the front face of the disc sample. The transient back-face temperature was monitored using a liquid-nitrogen-cooled infrared detector (Hg–Cd–Te) connected to an amplifier and a storage oscilloscope. The temperature–time data were analysed using Degiovanni's method,¹⁸ which takes into account the effect of heat losses on the value of thermal diffusivity. The

thermal conductivity (λ) was then calculated from the expression:

$$\lambda = \rho c \alpha \quad (1)$$

where α is the thermal diffusivity, c is the specific heat and ρ is the bulk density.

3. Results and discussion

3.1. Structure and microstructure

According to differential thermal analysis, four events occur during the thermal treatment of kaolin at approximately 500, 1000, 1200 and 1300 °C, related to structural changes of the clay.⁶ The X-ray diffraction diagram indicates the green body is well crystallised corresponding to hydrated aluminium silicate. Between 400 and 600 °C, dehydroxylation takes place, i.e. the structure loses its hydroxyl groups. No crystallised phases can be detected even though the layer structure is maintained in a distorted form called metakaolin. Close to 1000 °C, there is further structural reorganisation. First below 1200 °C, primary mullite crystallises inside the platelets.⁷ Then needle like mullite crystals are formed between 1225 and 1275 °C. Cristobalite appears at approximately 1300 °C (Fig. 1). Porosity evolves from 40% for green bodies to 4% for samples subjected to a thermal treatment at 1400 °C (Table 1).

Fig. 2(a)–(c) are micrographs of kaolin treated at 1050 and 1250 °C. After a treatment at 1050 °C kaolin still has a layered structure similar to the green body. The microstructure of a sample treated at 1250 °C is more complex, because it consists of thin needle like crystals of mullite, an amorphous phase and some remaining regions with the layered structure. It corresponds to an intermediate situation. The microstructures of samples treated

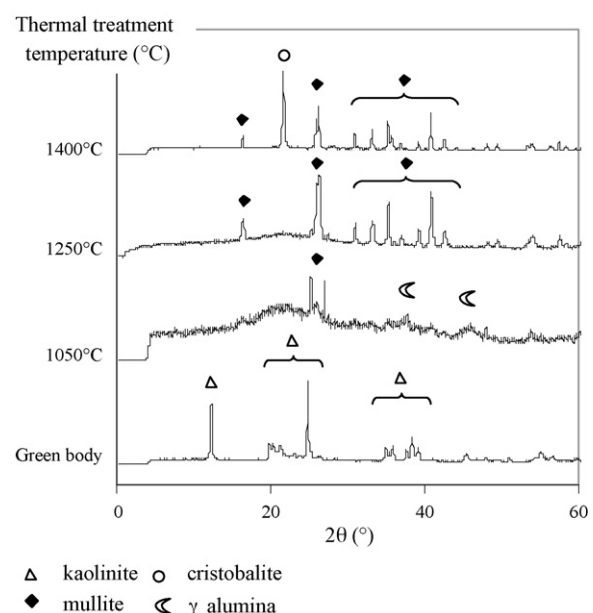


Fig. 1. XRD patterns for kaolin clay as a green body and with thermal treatment 1050, 1250 and 1400 °C.

Table 1
Major phases detected by X-ray diffraction and measured porosity for each sample

Thermal treatment temperature (°C)	Major phases	Porosity (%)
700	Amorphous	40
1050	Amorphous	38
1250	Amorphous, mullite	27
1300	Mullite, cristobalite	8.4
1350	Mullite, cristobalite	7
1400	Mullite, cristobalite	4

at 1350 and 1400 °C are no longer layered (Fig. 2(d)). Even though the distribution of sizes of needle like crystals of mullite is rather wide, the average size has increased compared to lower temperature thermal treatment.

3.2. Specific heat

In addition to the role for energy exchanges of a ceramic object during firing, knowledge of the specific heat for a given sample is necessary information for the evaluation of the thermal conductivity by the laser flash method. In general, the specific

heat of a material constituted of different solid phases can be calculated using the rule of mixtures. The rule of mixtures also gives a useful approximation for a material of unknown specific heat providing its chemical composition can be broken up into constituent parts with known values. In fact, with respect to the chemical composition of metakaolin, there is less than 2% difference between the calculated specific heat values for a mixture of mullite and cristobalite and that for a mixture of alumina and silica in the form of quartz. To test this idea, the specific heat of a sample treated at 1400 °C was measured between 350 and 1150 °C by calorimetry. Table 2 shows that the predicted values are in close agreement with experimental values for 350 °C and above. However, according to literature,¹⁴ the specific heat of metakaolin at room temperature is 1006 J kg⁻¹ K⁻¹ which is 30% higher than that calculated by the rule of mixtures, i.e. 750 J kg⁻¹ K⁻¹ (Fig. 3). The difference can be understood qualitatively using Debye's original model of the heat capacity. In this approach the temperature region, where specific heat increases strongly, is determined by a characteristic parameter for the crystalline phase called the Debye temperature (θ_D). θ_D depends on the atomic concentration and the speed of propagation of the acoustic lattice vibrations (Fig. 4). In essence the Debye temper-

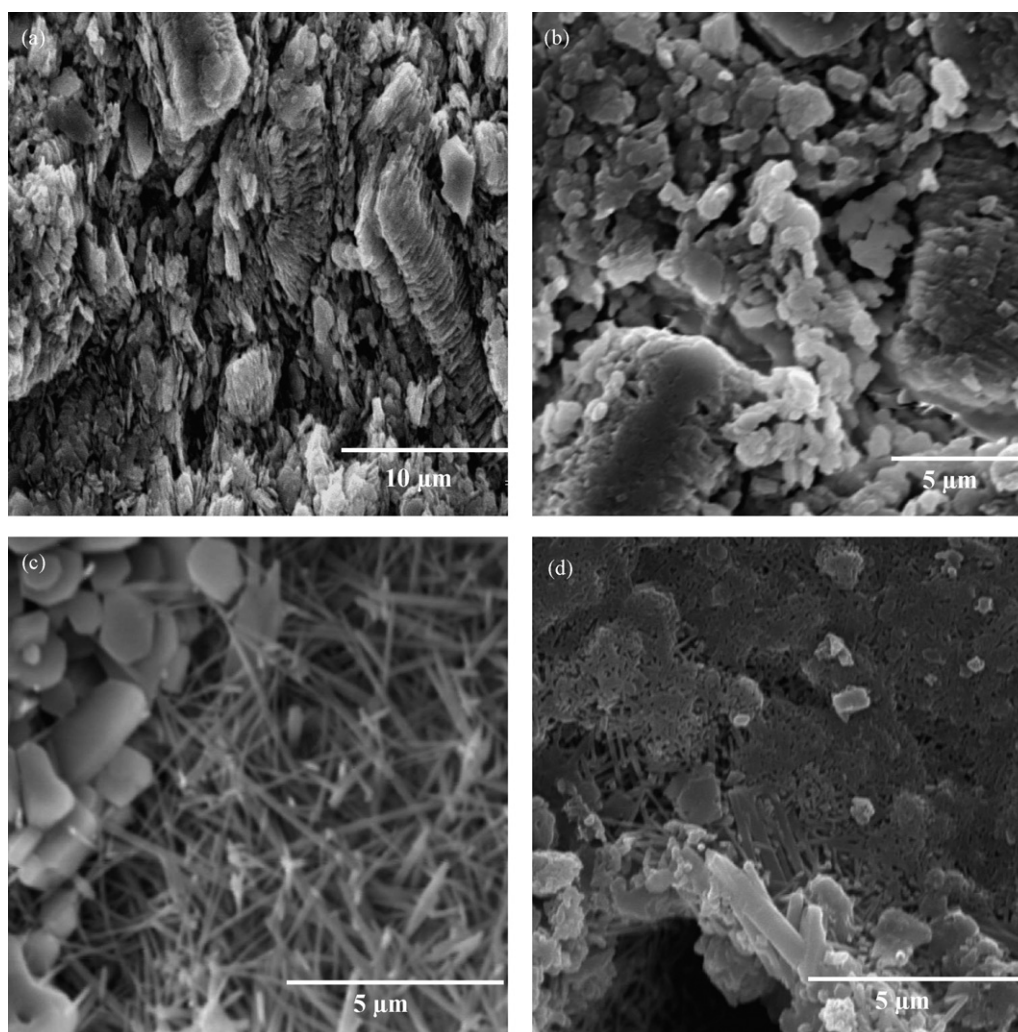


Fig. 2. Micrograph of kaolin treated at 1050 °C (a), 1250 °C (b and c) and 1400 °C (d).

Table 2
Comparison between measured and calculated specific heat values for kaolin treated at 1400 °C

T (°C)	Specific Heat (J kg ⁻¹ K ⁻¹)	
	Calorimeter	Rule of mixtures
350	1095	1081
450	1132	1119
550	1161	1147
650	1179	1169
750	1200	1187
900	1226	1209
1000	1245	1222
1100	1260	1232
1200	1272	1244

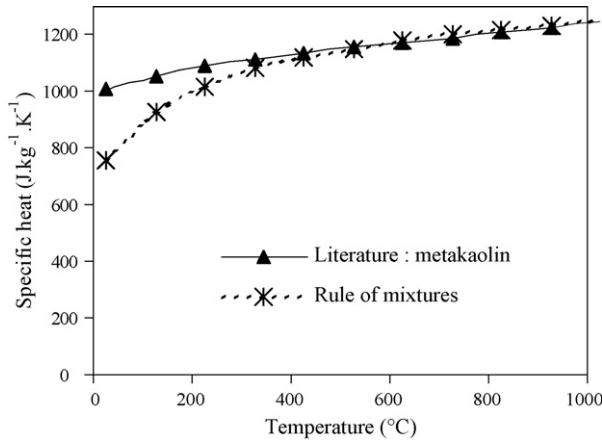


Fig. 3. Comparison between the values of specific heat for metakaolin from literature and those calculated with the rule of mixtures.

ature is high when the structure is stiff. After dehydroxylation, there is no longer “hydrogen bonding” between layers. This means, for metakaolin, the Debye temperature should be lower than for crystalline phases of alumina or silica. The approach using the rule of mixtures does not take this specific aspect of change in the Debye temperature into account. Since after firing at 1050 °C, the clay maintains a layered structure, specific heat

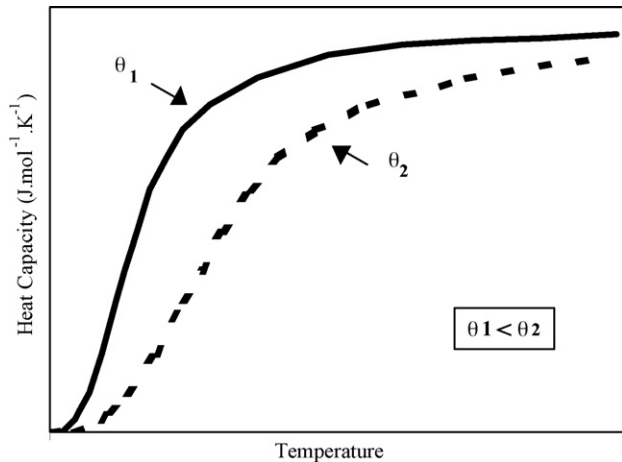


Fig. 4. Evolution of heat capacity as a function of temperature following Debye's model. The origin of the temperature axis is at $T = -273.15$ °C.

values given for metakaolin in literature¹⁴ are used in this work for samples fired at 700 and 1050 °C (Fig. 2(a)). SEM observations reveal that for clay fired at 1250 °C and above, the layer structure is progressively replaced by other forms of crystallite and glassy phase (Fig. 2(c) and (d)). Indeed the X-ray studies indicate that there is formation of mullite and cristobalite (Fig. 1). For these samples treated at 1250 °C and above, values obtained with the rule of mixtures were considered to be the relevant approximation.

3.3. Evolution in thermal conductivity

The thermal conductivity of the samples was measured between room temperature and 500 °C (Fig. 5). These samples treated at different temperatures do not contain the same amount of porosity. To compare data for equivalent fully dense materials, the solid phase, composed of grains and grain boundaries, is assumed to behave as a homogeneous medium at the scale of the pores. In a similar way to previous work on alumina and zirconia,^{19,20} Landauer's effective medium expression²¹ can then be applied to our samples to predict the thermal conductivity of the equivalent 100% dense solid phase λ_s with the equation:

$$\lambda_s = \frac{2\lambda^2 - \lambda\lambda_p(3v_p - 1)}{\lambda_p + \lambda(3v_s - 1)} \quad (2)$$

where λ is the measured thermal conductivity, λ_p is the thermal conductivity of the pore phase, v_p is the pore volume fraction and v_s is the solid phase volume fraction. The measured values and the predicted solid phase thermal conductivities of the samples at room temperature are given in Table 3. These show a significant increase of the room temperature thermal conductivity with

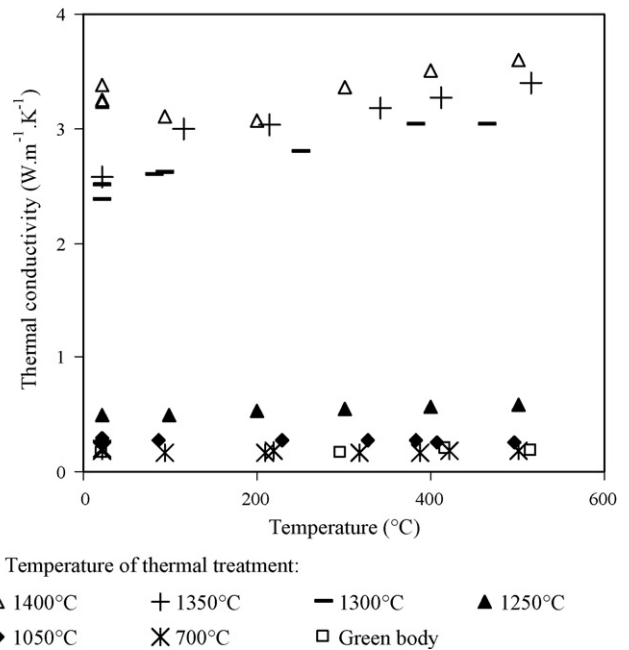


Fig. 5. Measured values of thermal conductivity between room temperature and 500 °C for kaolin clay as a green body and with thermal treatment 700, 1050, 1250, 1300, 1350 and 1400 °C.

Table 3

Values of measured thermal conductivity (λ) and predicted solid phase conductivity (λ_s) at room temperature

Thermal treatment temperature (°C)	λ ($\text{W m}^{-1} \text{K}^{-1}$)	λ_s ($\text{W m}^{-1} \text{K}^{-1}$)
–	0.17	0.34
700	0.18	0.39
1050	0.27	0.56
1250	0.49	0.80
1300	2.4	2.7
1350	2.6	2.9
1400	3.2	3.2

thermal treatment temperature, especially above 1300 °C, which cannot be explained uniquely by the decrease of the amount of porosity. Furthermore the experimental results show that for all the thermal treatments of kaolin, the thermal conductivity is constant or slightly increases with temperature. This behaviour, which is not modified significantly after correction of the porosity using Eq. (2), contrasts to the general case of a crystalline solid phase where thermal conductivity decreases with temperature due to phonon–phonon scattering. In fact for the samples with prior thermal treatment at 1400 °C, there is a small apparent decrease in thermal conductivity from room temperature to 200 °C, but it may just be an artefact of dispersion in the experimental data.

The green body and the sample treated at 700 °C, that is metakaolin, exhibit almost the same value of thermal conductivity. This means that dehydroxylation has no influence on the thermal conductivity. The insulating character of these three samples ($\lambda_s < 0.4 \text{ W m}^{-1} \text{ K}^{-1}$) can be attributed to the microstructural organisation of the kaolin clay in the form of small platelets with many interfaces. According to previous studies,^{22–24} above $\theta_D/2$, the thermal resistance attributed to the grain boundaries is virtually constant when temperature increases. The predominant effect of the interfaces can explain why even the thermal conductivity of the well-crystallised green body is almost constant between room temperature and 500 °C. For samples treated at 1050 °C, the layered structure is maintained. The slight increase in the room temperature value of the predicted solid phase thermal conductivity could then be explained by structural reorganisation and a consequence of the crystallisation inside platelets of primary mullite. At 1250 °C the exothermic phenomena which corresponds to the formation of needle like mullite crystals is not finished, whereas it is complete at 1300 °C.⁶ This suggests that the significant increase of thermal conductivity between 1250 and 1300 °C is a consequence of mullite formation and the disappearance of the layered structure. For these samples consisting of a mixture of crystallised and amorphous phases a slight increase of the thermal conductivity with temperature is still observed. To understand this phenomenon a cubic shaped crystal of mullite surrounded by a uniform layer of an amorphous phase has been considered (Fig. 6). Using a model of resistors in parallel and series, the thermal conductivity of this system is given by:

$$\lambda = \frac{e}{a} \lambda_G + \frac{be}{a^2} \lambda_G + \frac{c^2}{a} \frac{\lambda_G \lambda_M}{e \lambda_M + b \lambda_G} \quad (3)$$

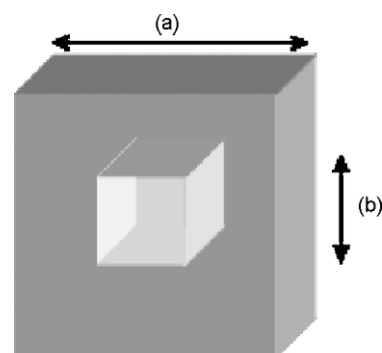


Fig. 6. Sketch: mullite crystal surrounded by amorphous phase.

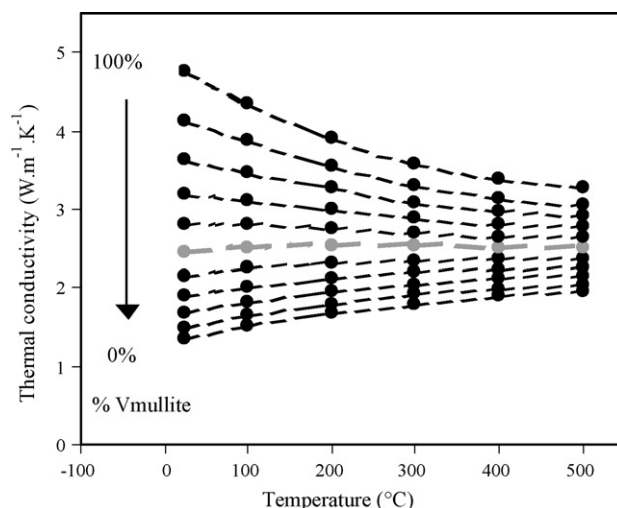


Fig. 7. Calculated thermal conductivity values for different volume fractions of mullite (100, 90, ..., 10, 0%) in an amorphous phase matrix.

where λ_M is the thermal conductivity of mullite,²⁵ λ_G is the thermal conductivity of the silicate glassy phase,²⁶ a and b are defined in Fig. 6 and $e = a - b$.

The evolution of the calculated thermal conductivity as a function of temperature for different volume fractions of the mullite crystal is shown in Fig. 7. The thermal conductivity increases with temperature when the volume fraction of the amorphous phase is greater than 50%. We deduce that for thermally treated kaolin which contains both crystalline and amorphous phases, the amorphous phase which surrounds the crystallites, controls the thermal conductivity and its behaviour with temperature.

4. Conclusion

During the thermal treatment of kaolin, the microstructure exhibits strong changes. The amount of porosity decreases from 40 to 4% whereas at the same time there is formation of an amorphous phase and crystals of mullite and cristobalite which replace the layered structure. This implies a significant decrease in the specific heat at room temperature from 1006 $\text{J kg}^{-1} \text{K}^{-1}$ for metakaolin to 750 $\text{J kg}^{-1} \text{K}^{-1}$ for a mixture of amorphous phase and crystalline phases. The thermal conductivity of the fully dense solid phase is also very sensitive to this structural

and microstructural evolution. It increases by a factor of 10 from $0.3 \text{ W m}^{-1} \text{ K}^{-1}$ for the green body to greater than $3 \text{ W m}^{-1} \text{ K}^{-1}$ with the crystallisation of mullite and cristobalite.

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