Standard Experimental Report
(All fields are mandatory)

Proposal title: ***High-temperature in-situ study of texturing and topotactic mullite crystallization within phyllosilicate-based textured ceramics***
Proposal number: ***20171337***
Beamline: ***BM02***
Shifts: ***15***
Date(s) of experiment: from: *2018, June 21* to: *2018, June 26*
Date of report: ***2018, November 5***

- Objective & expected results (less than 10 lines): **-**

We have explored recently the possibility to combine kaolinite with halloysite [1] or montmorillonite [2] in order to manufacture textured ceramics with enhanced mechanical properties. Our objective was to study the role of the clay particles shape and the sintering temperature on the structural evolution of phyllosilicate-based ceramic compounds (shaped by tape casting), using *in situ* high-temperature X-ray diffraction (XRD) measurements. The experiments were performed under a heating rate of 20°C/min within a furnace (Fig. 1) developed in the frame of the QMAX reasearch program (ANR-09-NANO-031-01), available at the BM02 beamline. The experiments were directed on two main scientific points:
(1) the dehydroxylation process of the clay minerals (kaolinite and halloysite) which occurs between 400°C and 800°C;
(2) the crystallization of mullite, between 900 and 1400°C (also isotherms at 1225°C for 8h).

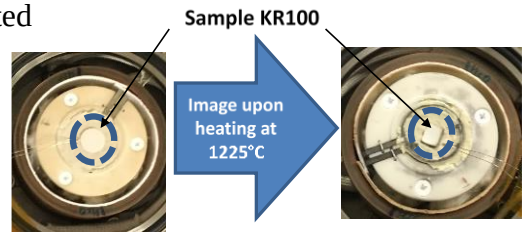
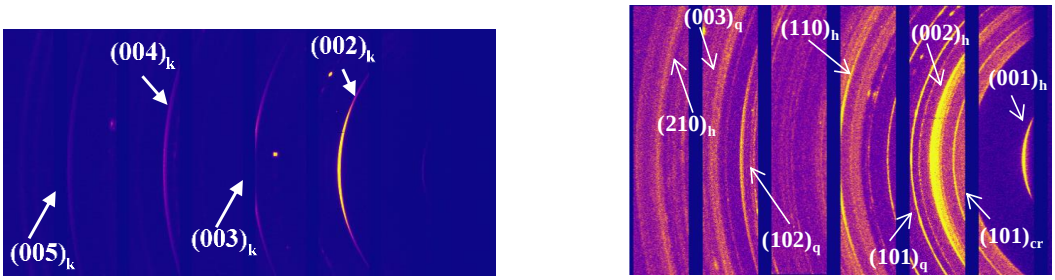


Fig. 1. Pictures illustrating the sample set-up within the furnace

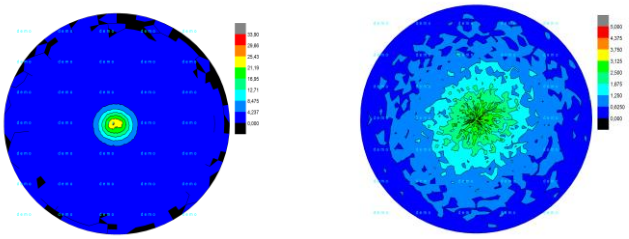
- Results and the conclusions of the study (main part): **-**

2D XRD maps were recorded at 17.9 keV very near to the zirconium absorption K-edge. Emphasis was led on two kaolins (KRG100 and KCS100) and a halloysite (H100). Typical 2D map obtained with the KRG100 and the H100 samples are presented on Fig. 2. As expected, the kaolin sample exhibited (00l) texture (Fig.2a) with respect to the sample surface. As evidenced on the (002) pole figures reported on Fig. 3, due to the tubular-shape of its particles, the sample H100 showed a less prononced texture with respect to the same crystallographic axis (Fig. 2b)
In order to take into account the textural effect, the incidence angle of the primary X-ray beam onto the sample was fixed at temperature up to 800°C in agreement with the Bragg angle of the (00l) kaolinite (or halloysite when indicated) planes, and at higher temperature (above 800°C) with respect to the Bragg angle of the mullite (120) diffraction peak. All these patterns were collected and analyzed in order to give a deep insight to the evolution of the texture in clay-based tapes depending on the firing conditions (temperature and heating rate) and the influence of the initial texture of the clay minerals. The obtained results will be used to probe the structural organization of the clay minerals within the initial tapes and to follow *in situ* the topotactic crystallization of mullite crystals upon heating up to 1400 °C. Experiments will allow correlating the crystallization and growth of mullite crystals with both the initial texture of clay minerals and the substitution of kaolinite by halloysite.



a) Kaolin sample KRG100 *b) Halloysite sample H100*

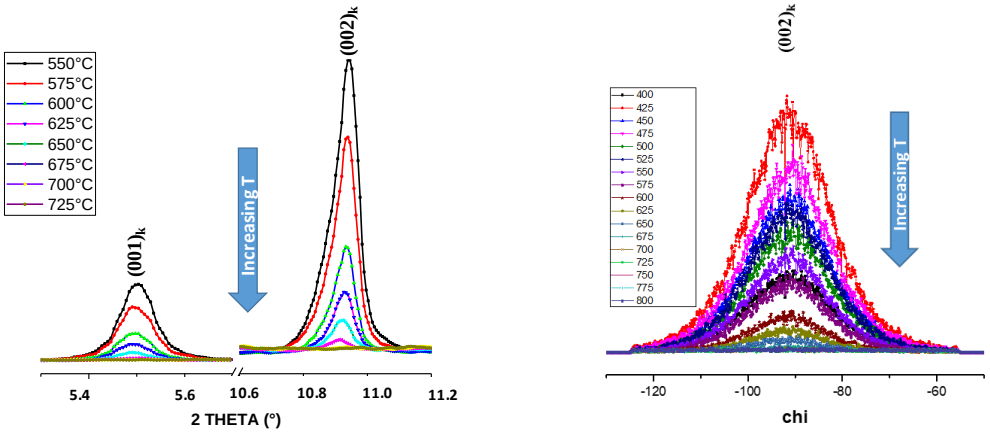
Fig. 2. 2D map recorded at room temperature (RT)



a) ***b)***

Fig. 3. (002) pole figures of a) kaolin KRG100 and b) halloysite H100 at RT

Fig. 4.a) illustrates the variation of the main (00l) peaks of the kaolinite phase during the dehydroxylation. Indeed, the vanishing of these peaks proceeds gradually from 450°C to 700°C. This trend is a new input regarding the study of the dehydroxylation process of kaolinite. The literature was considering that during this dehydroxylation, the XRD peaks of kaolinite disappeared abruptly at 550°C [3, 4, 5]. The difference with halloysite was noted according to the final temperature of the amorphization of halloysite phase (close to 650°C, patterns are not shown here). Furthermore, the texture within the KRG100 sample was preserved upon the dehydroxylation as assessed through the plot of the evolution of the $(002)_K$ peak intensity in the temperature range 400°C – 800°C as a function of the azimuthal angle χ (Fig. 4.b)).

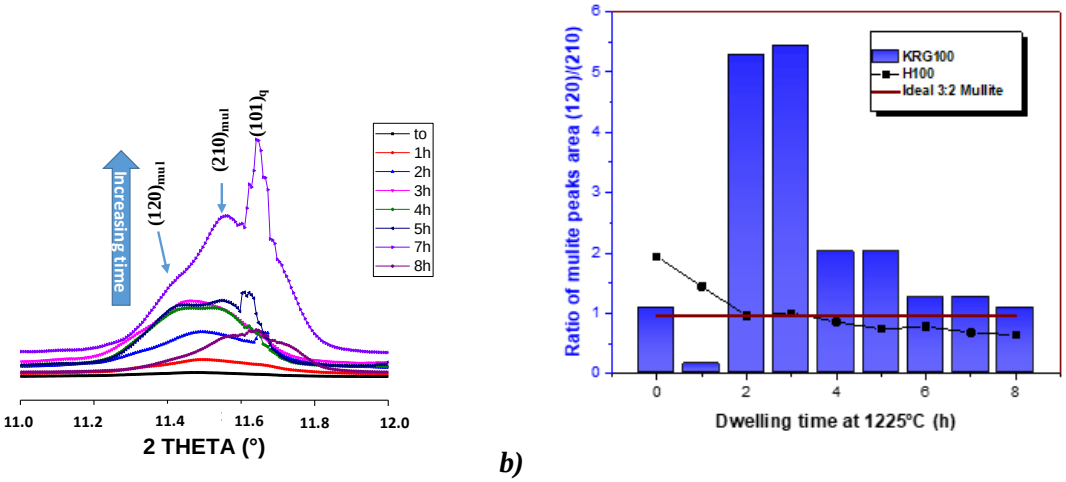


a) ***b)***

Fig. 4. (a) part of the 1D XRD patterns of the sample KRG100 with increasing dehydroxylation temperature; and (b) evidence of the texture of the kaolin sample KRG100 using the evolution of the peak intensity with respect to χ (azimuthal angle) during the dehydroxylation

After the amorphization observed in the various samples, the presence of transitory spinel like phases seemed to occur in the range 1000°C – 1150°C. Besides, the formation of mullite was detected at higher temperatures. The isothermal 1D patterns of KRG100 sample performed at 1225°C, are presented on Fig. 5.a) The intensity of the (120) and (210) diffraction peaks of mullite are increased with the increase of soaking time. Moreover, the relative intensities of the

mullite doublet ((120) and (210)) appeared to vary significantly with time (Fig. 5.b)). The latter behavior appears more pronounced for KRG100 than for H100, and is relevant with a time-dependent stoichiometry or texture of mullite in the early age of the crystallization. These results are consistent with the expected relation between the initial kaolinite texture and the newly formed mullite crystallites as well as the amount of mullite. The detailed analyses of the XRD patterns during the crystallization of mullite within the samples will also bring some useful hints regarding the crystallization kinetics in halloysite and kaolin-based samples.



a) *b)*

Fig. 5. a)1D XRD patterns related to the isothermal crystallization of mullite in the sample KRG100 at 1225 °C; b) Intensity ratio of (120) and (210) peaks of mullite into the KGR100 and H100 samples during the isothermal treatment performed at 1225 °C compared to the same ratio for the ideal 3:2 mullite

We acknowledge the ESRF and CRG for allowing us to perform these powerful experiments devoted to the understanding of the interplay between amorphization of phyllosilicate raw materials and their subsequent structural reorganization regarding mullite crystallization processes.

References

[1] N. Houta G.L. Lecomte-Nana, N. Tessier-Doyen, C. S. Peyratout, *Dispersion of phyllosilicates in aqueous suspensions: role of the nature and amount of surfactant*, Journal of Colloid & Interface Science, 423 (2014) 67-74.

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[3] P. Ptáček, T. Opravil, F. Šoukal, J. Brandštetr, J. Havlica, J. Másilko, *HT-XRD non-isothermal kinetics study of delamination of kaolinite from termite mound*, Applied Clay Science 95 (2014) 146–149.

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[5] N. Tezuka, I.-M. Low, I.J. Davies, M. Prior, A. Studer, *In situ neutron diffraction investigation on the phase transformation sequence of kaolinite and halloysite to mullite*, Physica B 385–386 (2006) 555–557.

- Justification and comments about the use of beam time (5 lines max.): **-**

The beamline BM02 was the most appriopriate line regarding our experiments requirements, namely the in-situ high resolution XRD at temperatures up to 1400°C. We were able to characterize the crystallization of mullite in the range 1225°C to 1400°C through isothermal measurements. Moreover, this beamline allows to perform rapid heating rate for dynamic and isotermal experiments.

- Publication(s): **-**

We are planning to submit a contribution to the upcoming Euroclay2019, in addition, we are working with these results in order to propose a scientific paper during year 2019.