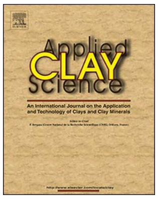
Applied Clay Science 157 (2018) 19–23

Contents lists available at ScienceDirect

Applied Clay Science

journal homepage: www.elsevier.com/locate/clay



Research paper

Temperature dependence of the AC conductivity of illitic clay

Štefan Csáki[a,b,*], Ján Ondruška[a], Viera Trnovcová[a], Igor Štubňa[a], Patrik Dobroň[b], Libor Vozár[a]

[a] Constantine the Philosopher University in Nitra, Faculty of Natural Sciences, Department of Physics, Tr. A. Hlinku 1, 949 74 Nitra, Slovak Republic
[b] Charles University, Faculty of Mathematics and Physics, Department of Physics of Materials, Ke Karlovu 5, 121 16 Prague, Czech Republic

ARTICLE INFO

Keywords:
Electrical conductivity
Illite
Ionic conductivity
Clay

ABSTRACT

Electrical conductivity measurement was used to characterize thermophysical processes occurring in illitic clay during firing. In this study, illitic clay was subjected to heating up to 1100 °C. The AC conductivity was measured at 10 different frequencies, ranging from 500 Hz up to 2 MHz. In the low-temperature interval (< 250 °C) and during dehydroxylation (from 450 °C to 750 °C), H^+ and OH^- ions were the dominant charge carriers. Above 600 °C, the mobility of alkali ions was high enough to enable them to contribute to conductivity. Formation of glassy phase at high temperature rapidly increases conductivity. The conduction activation energies (E_A) were calculated during a second firing. Above 350 °C, the values of E_A lay in the interval between 0.79 eV (500 Hz) and 0.66 eV (2 MHz), which correspond to the conduction E_A of alkali ions in an amorphous matrix. The responsible conduction mechanism was identified to be ion hopping.

1. Introduction

Clay minerals are of special importance for a wide range of industries (e.g. ceramics, building, etc.). The structure of these minerals manifests several modifications. Illite has a layered structure, where an octahedral sheet is located between two tetrahedral sheets forming a T-O-T layer. Between these layers, K^+ ions are situated. During heating, several thermophysical processes take place. Firstly, the physically bound water is released. This reaction is followed by the dehydroxylation, during which the chemically bound OH^- groups are removed. At high temperatures, illite undergoes a phase change and a glassy phase appears, which promotes the sintering process (Húlan et al., 2015, 2017).

The electrical properties of clays are frequently studied in relation to the moisture content, e.g. (Chudinova, 2009; Ishida et al., 2000; Kaden et al., 2013). Contrary to that, only a few papers are devoted to the electric, as well as dielectric properties of clays during firing e.g. (Kriaa et al., 2014; Podoba et al., 2014; Trnovcová et al., 2012). The measurement of the electrical conductivity can provide an information on the ion movement (Podoba et al., 2014), as well as on polarization effects (Ondruška et al., 2015a, 2017) during thermophysical reactions. Previous studies showed (Lerdprom et al., 2017; Ondruška et al., 2015b; Podoba et al., 2014), that in different temperature intervals the dominant charge carriers can vary. It has been shown, that ionic conductivity is the dominant conduction mechanism in these materials (Kasrani et al., 2016; Kriaa et al., 2014; Sidebottom et al., 1995; Wang and Xiao, 2002).

The frequency dependence of dielectric properties of clays has been studied by several authors, e.g. (Bore et al., 2017; Douiri et al., 2017; Ishida et al., 2000). The frequency dependence of the AC conductivity can be described by Jonscher's power-law (Jonscher, 1983). Based on this power-law, it was found that the ionic conduction occurred via hopping mechanism. In the low-frequency region, below a certain frequency, long-range transport of ions is responsible for the conductivity. As the frequency increases, the short-range interactions become important (Kriaa et al., 2014; Roy et al., 2013) and a localized ion hopping dominates.

In this study, the AC conductivity measurement in the frequency range from 500 Hz to 2 MHz was performed on illitic clay during firing in order to reveal dominant conductivity mechanisms. To support the results, thermal analyses – differential thermal analysis (DTA), thermogravimetry (TG), and thermodilatometry (DIL) – were carried out. In addition, the temperature and frequency dependence of the AC conductivity of fired samples was measured. According to the authors' knowledge, the description of thermophysical processes via AC conductivity has not been done before. Measurement of the electrical properties allows to better understand the conduction mechanism. Moreover, the results can be used to help to designate a suitable firing regime to achieve flash sintering.

2. Experimental

The illitic clay (containing 80 mass% of illite) used in this study, is originated in Miskolc region, Hungary. The chemical composition of the

---

* Corresponding author at: Constantine the Philosopher University in Nitra, Faculty of Natural Sciences, Department of Physics, Tr. A. Hlinku 1, 949 74 Nitra, Slovak Republic.
E-mail address: stefan.csaki@ukf.sk (Š. Csáki).

https://doi.org/10.1016/j.clay.2018.02.026
Received 13 October 2017; Received in revised form 2 February 2018; Accepted 15 February 2018

Table 1
Chemical composition of illite from Füzérradvány, Hungary (in wt%).

SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	K_2O	Na_2O	LOI
58.0	24.0	0.6	0.05	0.38	1.70	7.85	0.10	7.3

clay is shown in Table 1. The M1 - polytype of illite was confirmed by Gualtieri and Ferrari (2006). The raw material was crushed and milled to pass through the 100 µm mesh. In the next step distilled water was added and samples were manufactured from the obtained plastic mass.

DTA and TG were performed on compact samples using the upgraded Derivatograph (MOM Budapest) analyzer (Podoba et al., 2012). Samples had a rectangular shape of dimensions (11 × 11 × 16) mm. For DTA, the reference sample of the same dimensions was made from pressed Al_2O_3 powder.

DIL was carried out on samples of rectangular shape (8 × 8 × 20) mm using the Netzsch DIL 402C apparatus in a dynamic N_2 flow (flow rate 40 ml/min).

Microstructure of the raw sample was observed using the electron microscope Zeiss Auriga with an accelerating voltage of 3 kV. The microstructure of fired samples was studied by the FEI Quanta™ 200FX in a low vacuum mode (100 Pa) with an accelerating voltage 10 kV. The fired samples were mechanically polished and cleaned in an ultrasonic bath.

The AC conductivity measurements were carried out on rectangular samples, in which two wire electrodes (ϕ 0.4 mm) were inserted (Štubňa et al., 2015). The samples were placed into the measurement cell and connected to the TEGAM 3550 LCR meter. The sample resistance was recorded during heating at 10 frequencies. From the measured resistance R_p the electrical conductivity (σ_{AC}) was determined as

$$\sigma_{AC} = \frac{1}{R_p}\beta$$

where β is the geometric factor, which was determined experimentally (Štubňa et al., 2015).

The same heating regime (5 °C min^{-1} up to 1100 °C) was used for all measurements to avoid the influence of different heating rates. Prior to the measurement, the samples were heated up to 120 °C and a 60 min holding time was applied to remove the technical water (introduced during the preparation) from the samples. At the highest temperature, a 5 min soaking time was applied. After cooling down the samples in the measurement cell, a second run up to 1100 °C was done.

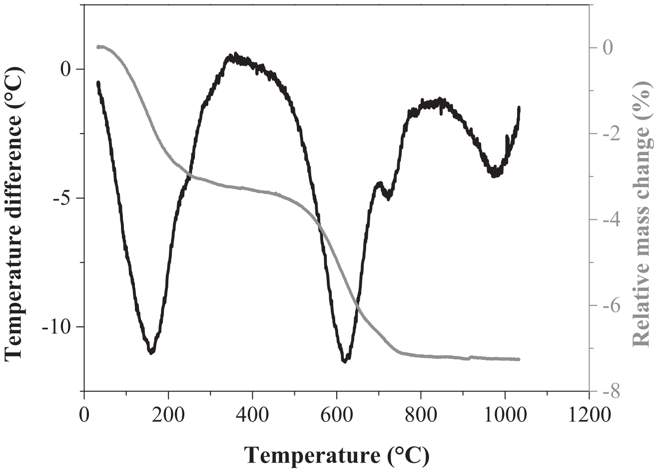


Fig. 1. DTA and TG curves of the raw sample.

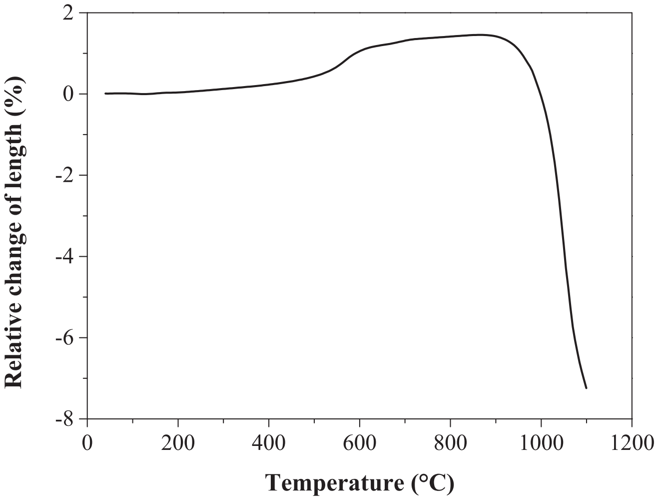


Fig. 2. Thermodilatometric curve of the sample.

3. Results and discussion

The DTA (Fig. 1) exhibited 3 significant endothermic reactions. The first peak is observed from 30 °C up to ~300 °C. In this temperature region, the removal of the physically bound water (PBW) takes place. This process is accompanied by a 5% decrease in the sample mass (Fig. 1). However, the dimension of the sample remains almost unchanged (Fig. 2). The second endotherm reaction, occurring in the temperature interval from 450 °C to 750 °C, is dehydroxylation. The dehydroxylation of illite is a 2-step process (Gualtieri and Ferrari, 2006), the two steps are spaced apart by ~80 °C. In the first step, the dehydroxylation of the illite-M1 takes place, while in the second step the illite-M2 loses its chemically bound OH⁻ groups (Húlan et al., 2017). The driving force of the process is diffusion (Gualtieri and Ferrari, 2006). In the corresponding temperature interval, the mass of samples decreased by 6.5%. The process is also accompanied by a 1% relative expansion of the sample. After finishing the dehydroxylation process, high-temperature phase transformations were observed in the sample. The mass of the sample did not change significantly after dehydroxylation. Once the dehydroxylation is finished, the illite is transformed into a dehydroxylated phase. The XRD reflections owing to the illite phase decrease, but do not vanish up to 850 °C (Gaied et al., 2011; Húlan et al., 2015). The decrease of XRD reflections after dehydroxylation is connected with the creation of amorphous phase. A slight expansion of the samples' dimensions is observed up to 950 °C, owing to the expansion of the *b* and *c* axes and the simultaneous shrinkage of *a* axis and β angle of the crystals of dehydroxylated illite (Wang et al., 2017). The above described expansion and the decrease in the samples mass (Fig. 1) led to an increased porosity compared to that at room temperature (Húlan et al., 2015). A steep contraction of the sample dimensions is observable from 950 °C, which represents the beginning of the sintering process. The microstructure of the fired sample, compared to that of the raw one, is shown in Fig. 3.

Temperature dependence of the AC conductivity, at various frequencies, of the samples during thermal treatment is presented in Fig. 4. Below 230 °C, a peak is observed on the temperature dependence of the AC conductivity at all frequencies. This is related to the removal of the residual physically bound water. Although the samples were dried in the measurement cell for 1 h at 120 °C, H_2O molecules between T-O-T layers and H^+ or OH⁻ ions bound to the grain and pore surfaces remained in the samples (Drits and McCarty, 2007). The high values of the AC conductivity at these low temperatures thus can be related to the dielectric response of H^+ and OH⁻ ions created by a decomposition of the surface water, as well as to the interface polarization. Once the residual physically bound water was removed, the AC conductivity reached its minimum value. With increasing temperature (up to 450 °C)