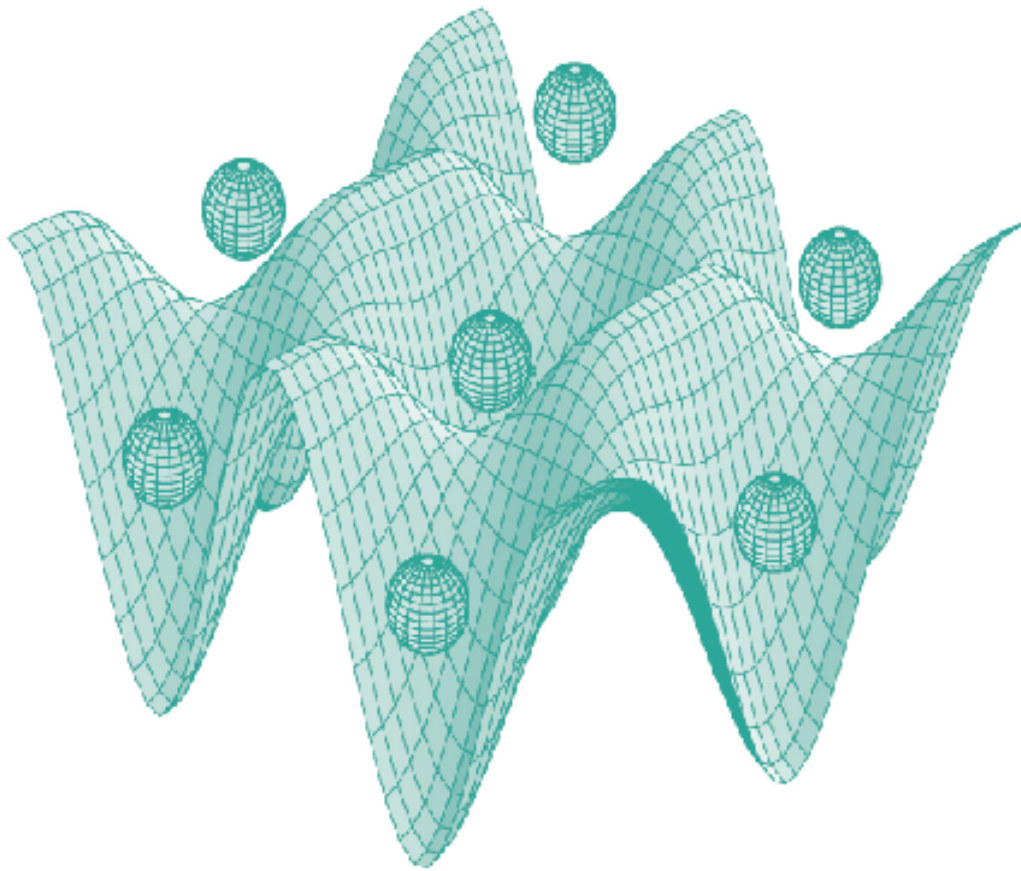




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STRUCTURAL CHANGES INDUCED IN MINERAL CLAYS BY HIGH TEMPERATURE HEAT TREATMENTS

M. TĂMĂȘAN¹, H. MOCUȚA¹, C. IONESCU², V. SIMON^{1*}

ABSTRACT. Thermal changes occurred during firing of clays in order to obtain ceramic samples are important for understanding their properties. In the present paper we report results obtained by thermogravimetric (TGA) and differential thermal analysis (DTA) as well as by X- ray diffraction (XRD) on low and high temperature heat treated clay samples used to produce black-ceramic. TGA and DTA data point out characteristic dehydroxylation and decomposition reactions, and only slight structural changes in the crystalline network up to 700 °C. For the samples heat treated 1100 °C and 1200 °C, the XRD results show the development of magnetite and/or maghemite crystalline phase.

Key words: Clays; heat treatment; structure; DTA; XRD.

1. Introduction

Natural clay minerals are well known and familiar from the earliest days of civilization. Because of their low cost, abundance in most continents of the world, high sorption properties and potential for ion exchange, clay materials are strong candidates as adsorbents. Clay materials possess a layered structure and are considered as host materials. They are classified by the differences in their layered structures. There are several classes of clays such as smectites (montmorillonite, saponite), mica (illite), kaolinite, serpentine, pyrophyllite (talc), vermiculite and sepiolite [1]. The adsorption properties result from a net negative charge on the structure of minerals. This negative charge gives clay the capability to adsorb positively charged species. Their sorption properties also come from their high surface area and high porosity [2]. Montmorillonite clay has the largest surface area, around 200 m²/g, and implicitly the highest cation exchange capacity, while the surface area of illite is only about tens of m²/g [3, 4].

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During the last decades, mineral clays attracted great interest due to their capacity to adsorb not only inorganic but also organic molecules, that was exploited in applications, such as adsorbents for pollutants [5-8], rheological control agents [9], reinforcing fillers for plastics [10], clay-based nanocomposites [11] and precursors for preparing mesoporous materials [12, 13].

This paper reports on structural changes caused by heat treatment applied at high temperatures on panonian age illite clay, with occurrence in Odorheiul Secuiesc area, Romania, as evidenced by thermal analysis, density measurements and X-ray diffraction analysis.

2. Experimental

The clay samples investigated were obtained from natural deposits of in Odorheiul Secuiesc area. This row clay is normally used in producing the traditional Marginea black-ceramic. The samples were washed, air-dried and sectioned as disks sized about 35x30x8 mm. Differential thermal analysis (DTA) and thermogravimetric analysis (DTA) were carried out on Shimadzu type derivatograph DTG-60H, with a heating rates of 5 °C/min using alumina open crucibles. The samples were heat treated at temperatures ranging between 700°C and 1200°C, for 2 hours, in air under normal pressure. The density of the samples was determined by Archimedes principle using the pan balance. The structure of the non-treated and heat treated samples was investigated by X-ray diffraction with a Shimadzu XRD-6000 diffractometer, using Cu-K_α radiation ($\lambda = 1.5418 \text{ \AA}$), with Ni-filter.

3. Results and discussion

Thermal analysis runs are given in Fig. 1. The DTA curve of starting material presents three peaks which indicate the thermal changes of the row material. The first endothermic peak corresponds to a large water loss starting at about 50 °C, which is attributed to moisture present in the sample. Another endothermic process takes place about 600 °C where dehydroxylation is substantially complete [14]. At the same time, the mass loss noticed starting with 600 °C could be related to the elimination of some gaseous species existing in these clay [15]. The weak exothermic event at 330 °C is expected to arise from slight structural changes in the crystalline network or combustion of some organic matter. The temperature at which ancient ceramics and pottery were fired is considered to vary over a wide range (600-1300°C) depending on the type of clay used and the kiln available, although firing temperatures only up to 300-400 °C have also been suggested [15].

For our sample, the grey colour of the non-heated clay changes to bright brown by heat treatment at 700 °C. By increasing the treatment temperature, the colour becomes more intense and changes to black for the sample heat treated at 1200 °C.

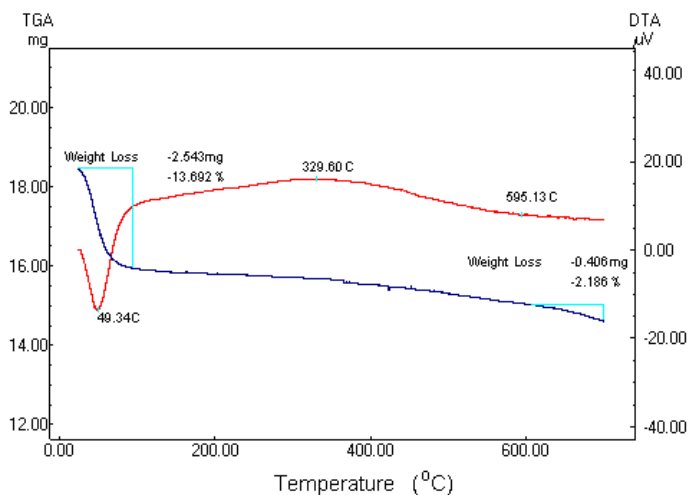


Fig. 1. Differential thermal analysis (DTA) and thermogravimetric (TGA) curves for the non-treated sample.

The change of the density after the applied heat treatments is displayed in Fig. 2. A weak decrease of the density is observed after heating at 700 °C, but this is very pronounced after the heat treatment applied at 800 °C. By further increasing of the treatment temperature, the density starts to enhance and a highly compacted sample results for the sample heat treated at 1200 °C.

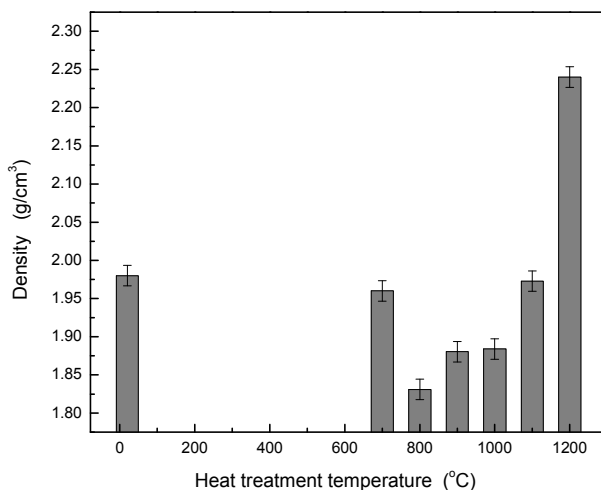


Fig. 2. The density of the row and heat treated samples.

The X-ray diffraction patterns are shown in Fig. 3. A typical illite diffraction pattern [16] with peaks at 8.67, 17.87, 27.83, 36, 37.5 and 45.3° is recorded from the raw clay sample. Beside the dominant illite phase, kaolinite and quartz components are also identified (Fig. 4). For the samples heat treated between 700 °C and 1100 °C the silica polymorph moganite is also present, as suggested by the new diffraction peak recorded at 19.7° [17]. The increasing crystallinity is shown by the sharpening, up to 1100 °C, of all diffraction peaks. The two hours heat treatment applied at high temperatures of 1100 °C and 1200 °C induce the crystallisation of hematite and magnetite on the account of the iron oxide contained in the clay [18]. The diffraction peaks recorded at 30.2 and 35.6° clearly point out the prevalence of magnetite in relation with the hematite, because hematite is mainly represented by the 33.2° diffraction peak. At the same time it is to take care on the fact that the crystal structure of maghemite ($\gamma\text{-Fe}_2\text{O}_3$) is similar to that of magnetite (Fe_3O_4). The main structural difference between maghemite and magnetite is the existence of vacancies in maghemite, which lowers the symmetry of maghemite (primitive Bravais lattice) with respect to magnetite (face-centered Bravais lattice). Further ordering of the vacancies results in a tetragonal superlattice structure with $c = 3a$ [19-21]. In general, solid-state oxidation of magnetite may result in maghemite formation. Because magnetite and maghemite are very similar in their structures and their XRD patterns, diffraction peaks from magnetite nearly overlap with those from maghemite. Unit cell parameters for magnetite- and maghemite-based cubic setting are 0.840 nm and 0.835 nm, respectively. A slight difference in the unit cell parameters results in a slight shift of all peaks from maghemite towards higher angles with respect to the peaks from magnetite [18]. When magnetite and maghemite coexist together, diffraction peak intensity and peak shape will change as their proportions change and it is difficult to identify them by using powder XRD analysis alone.

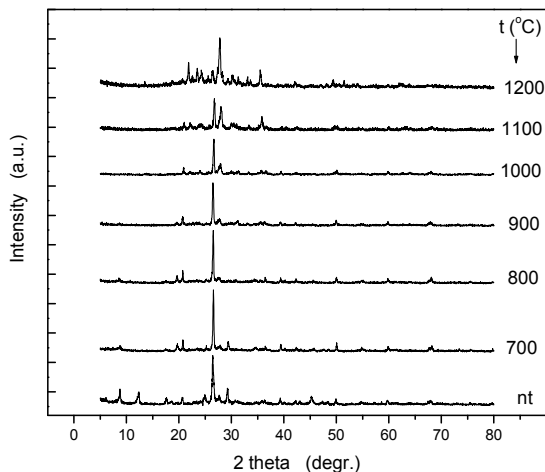


Fig. 3. X-ray diffractograms of non-treated (nt) and heat-treated samples.

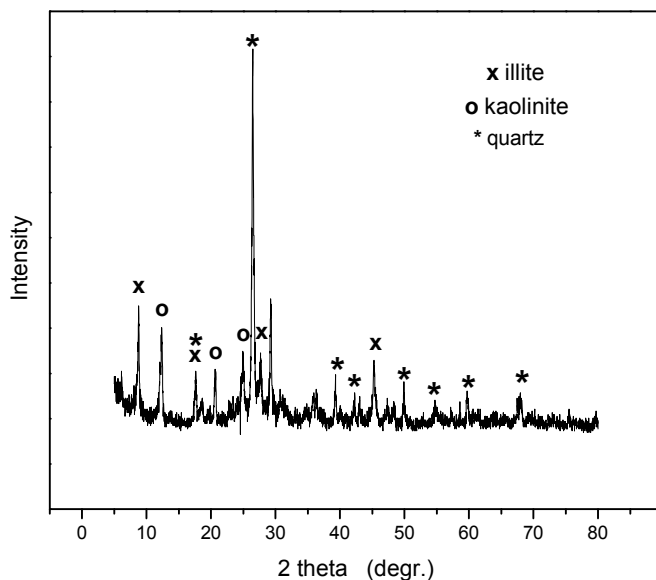


Fig. 4. X-ray diffraction pattern of row clay sample.

The development of magnetite and/or maghemite in our sample is additionally proved by the black colour of the sample heat treated at 1200 °C. At the same time, one remarks that this sample has the highest density (Fig. 2) and, as already mentioned, it has a glassy glint. A careful inspection/analysis of the corresponding XRD pattern (Fig. 3) evidences the appearance of a vitreous phase giving rise to a very large diffraction line in the 20-30° range of 2θ . Another remark refers to the slight width broadening of the diffraction lines, that denotes a diminishing of sample crystallinity.

4. Conclusions

The row mineral clay consists of a dominant illite phase, but kaolinite and quartz components are also identified in XRD pattern. DTG and DTA point out characteristic dehydroxylation and decomposition reactions, and only slight structural changes in the crystalline network up to 700 °C. For the samples heat treated at 1100 °C and 1200 °C, the XRD results show the development of magnetite and/or maghemite crystalline phase. Under normal heating conditions at 1200 °C for two hours, the colour of the grey row clay is changed to black and the sample achieves a glassy glint.

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