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# Effect of hydrothermal treatment on the structure of an aluminosilicate polymer

**Research Article**

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**Abstract:** The effect of hydrothermal treatment on the structure of an aluminosilicate polymer prepared by a polycondensation reaction between silicate and hydroxoaluminate in alkaline aqueous solution was studied. The structural changes were investigated using X-ray diffraction analysis, Fourier-transform infrared spectroscopy, scanning electron microscopy imaging and thermogravimetric analysis. The results indicated that the amorphous aluminosilicate polymer transformed into a crystalline product during the hydrothermal treatment at 145°C. The crystalline phase was identified as a mineral of the zeolite group, most likely phillipsite. This transformation required an alkaline environment during the hydrothermal treatment.

**Keywords:** *Aluminosilicate polymer • Zeolite • Hydrothermal treatment • Polycondensation • Geopolymerization*



## 1. Introduction

Products synthesized *via* chemical reactions in alkali environments from calcined kaolin or similar aluminosilicate materials can be divided, according to their crystallinity, into two main types: crystalline and amorphous. The crystalline products are synthetic zeolites; these materials consist fundamentally of a three-dimensional tetrahedral structure and usually exhibit a large number of micro-pores [1]. A wide variety of zeolite minerals can be found in nature. They are mostly formed from sediments in the presence of water under high pressure and temperature (*i.e.*, under hydrothermal conditions). The synthetic zeolites are produced from compounds that contain silica and alumina by heating with water in an autoclave (*i.e.*, also under hydrothermal conditions). Both natural and synthetic zeolites have a broad spectrum of applications. Zeolites can be used for aquarium cleaning, remediation of petroleum spills or drinking water filtration, in addition to their main applications in the chemical industry as sorbents and catalysts. They are also used for the neutralization of acidic soils and as a concrete admixture in the building industry [2]. Some zeolites were even added to livestock feed [3].

The amorphous products that can be prepared from raw aluminosilicate materials are mainly inorganic aluminosilicate polymers, also known as geopolymers [4]. In contrast to zeolites, the aluminosilicate polymers are usually prepared under atmospheric pressure and without heating or, in some cases, at a slightly increased temperature (up to 80°C) to accelerate the reaction [5]. The raw materials used are generally the same as for the synthesis of zeolites: materials with high contents of silica and alumina [6]. One of the most used raw materials for the synthesis of zeolites or geopolymers is calcined kaolin [7]. During the process of kaolin calcination, crystalline water contained in the kaolinite is lost and

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some structural changes occur that result in a higher reactivity of the material. The calcined kaolin is then mixed with an alkali hydroxide solution and eventually with water glass (an aqueous silicate solution), depending on the desired properties of the product and the composition of the raw materials [8]. The obtained mixture usually hardens in the open air without heating. In addition to natural minerals, certain waste materials, such as coal fly ash [9], bottom ash [10] or blast furnace slag [11] can also be used. Geopolymers can be used in many applications, including as substitutes for Portland cement and other traditional building materials, in the restoration of historical monuments [12], for the stabilization/solidification of hazardous waste [13], or for the construction of nuclear waste disposal sites [14]. Concretes prepared from geopolymers have better chemical and thermal resistance than those made from Portland cement, and their production consumes significantly less energy and emits less carbon dioxide [15]. Current research is being conducted also on the composite materials using the geopolymer matrix [16].

The mentioned types of synthetic aluminosilicate materials differ in their crystallinity, porosity and especially in their mechanical properties. Whereas the geopolymers can form monolithic solids with high compressive strength up to 100 MPa [17], the zeolites are entirely unsuitable as construction materials because they are usually formed as a powder or at most as a conglomerate with relatively low compressive strength. The question of whether the amorphous geopolymers can be transformed into crystalline zeolites is therefore important for some specific applications and has recently been studied [18]. Besides the X-ray diffraction (XRD) technique commonly used to determine the crystalline phase content, other instrumental methods, such as scanning electron microscopy (SEM) and nuclear magnetic resonance (NMR), can also be used to assess the crystallinity of the aluminosilicate materials [19].

Krivenko and Kovalchuk [20] have studied the behavior of geopolymers prepared from different raw materials. They heated the geopolymer samples first to 80°C under dry air or water vapor and later to 800–1000°C. Crystalline structures and different types of zeolites were observed; however, the crystallinity ratios were relatively low. Kolousek *et al.* [21] observed acceleration in the condensation of free Si–OH groups during the hydrothermal treatment of geopolymers, which resulted in an increase in the crystallinity and the partial transformation of the geopolymer into a zeolite. Zhang *et al.* [22] have reported a gradual increase of crystallinity in the geopolymer that was made from metakaolinite and cured at a temperature of 40°C; they also identified several types of zeolites in the crystalline phase. Another important finding was the marked influence of the composition of the reaction mixture on the crystallinity ratio. A significant increase in the crystallinity was observed for samples prepared with an addition of alkali hydroxide, whereas the addition of alkali silicate resulted mostly in no crystallinity increase. Villa *et al.* [23] have also investigated the reverse transformation of zeolites into geopolymers; however, the content of the crystalline phase in the resulting product was relatively high; the term “geopolymer” is therefore not a suitable name for the product.

In this paper, the hydrothermal treatment of the product prepared by the polycondensation reaction of silicate and hydroxoaluminate in aqueous alkaline solution [24] was investigated. The aim of this work is to investigate the effects of the hydrothermal treatment on the aluminosilicate polymer. On the assumption that the prepared aluminosilicate polymer is the same compound as the one that occurs in geopolymer concrete, the results should be applicable to the behavior of geopolymers.

## 2. Experimental procedure

### 2.1. Sample preparation

The aluminosilicate polymer was prepared by the reaction between hydroxoaluminate and silicate in aqueous alkaline solution. The hydroxoaluminate solution was prepared by dissolving 1 g of $KAl(SO_4)_2 \cdot 12\ H_2O$ in 25 mL of 1 mol $L^{-1}$ KOH. The silicate solution was prepared by dilution of 1.25 g of potassium water glass (containing 20.11% $SiO_2$ and 8.08% $K_2O$) in another 25 mL of 1 mol $L^{-1}$ KOH. Both solutions were heated at 30°C, mixed together and kept at 30°C until a gel formed. A part of the formed gel was washed out by mixing the gel with distilled water in a ratio of 100 mL of water to 10 mL of gel. After 1 h of mixing using a magnetic stirrer, the gel phase was left to sediment for 24 h and the water phase was extracted. The washing procedure was repeated five times. The washed gel was then dried at 105°C for 24 h. Another part of the gel was only dried and tested without washing. The samples of dried gel (xerogel), together with distilled water (1 mL of $H_2O$ per 1 g of xerogel), were dosed into steel pressure vessels coated with Teflon on the inner sides. The closed vessels were then heated at 145°C for 25 d while samples of the treated gels were collected in selected intervals. In the case of the hydrothermal treatment of the unwashed xerogel, the washing procedure was performed after the hydrothermal treatment.

**Table 1.** Chemical compositions of xerogels, expressed as the weight percentage of element oxides and loss on ignition.

| Xerogel type | $Al_2O_3$ [ % ] | $SiO_2$ [ % ] | $K_2O$ [ % ] | $SO_3$ [ % ] | LOI [ % ] |
|---|---|---|---|---|---|
| [a]Unheated, unwashed | 1.8 | 4.2 | 42.2 | 5.6 | 46.2 |
| [b]Unheated, washed | 22.2 | 44.1 | 18.7 | – | 15.1 |
| [b]Hydrothermally treated, washed | 20.3 | 46.2 | 20.3 | – | 13.1 |

*a - values calculated theoretically from the reaction mixture composition*
*b - values determined by XRF; loss on ignition measured at 650°C*

## 2.2. XRD analysis

The X-ray diffraction (XRD) spectra were measured using an X'Pert PRO spectrometer (PANalytical B.V., The Netherlands) equipped with a theta–theta goniometer, a Cu Kα radiation (λ=0.1542 nm) source and a PIXcel detector. All measurements were performed at ambient temperature in reflection mode at 40 kV and 30 mA with fixed slits in the range from 6 to 90° (2θ). The step size was 0.0131°, and the count time was 13.77 s per step.

## 2.3. XRF Analysis

The chemical composition of the samples was determined by an ElvaX Ser-01 (Elvatech, Ukraine) energy-dispersive X-ray fluorescence (XRF) spectrometer equipped with a Si pin-diode detector with electrical cooling *via* the Peltier effect, an active area of 7 $mm^2$, an 8-μm Be entrance window and an energetic resolution of 220 eV for $^{55}Fe$ Kα 5.9 keV. Energetic calibration was performed using a Ni/Fe/Mo reference sample. For the quantitative analysis, the spectrometer was calibrated by a set of 14 mixed calibration standards prepared from $SiO_2$, $Al_2O_3$ and $K_2CO_3$. The measurement was performed at a tube voltage 10 kV, a tube current 64 μA and with an effective exposure time 180 s.

## 2.4. FTIR Analysis

The prepared samples were analyzed by Fourier-transform infrared spectroscopy (FTIR) on a Nicolet IS10 spectrometer (Thermo Scientific, USA) in the range of 400-4000 $cm^{-1}$ using the KBr pellet technique. The OMNIC v. 8.1.210 software was used for the analysis of the FTIR spectra.

## 2.5. SEM Imaging

Scanning electron microscopy (SEM) images were obtained using a VEGA II LMU electron microscope (Tescan, USA).

## 2.6. Thermogravimetric analysis

Thermogravimetric analysis (TGA) was carried out at a heating rate of 10°C $min^{-1}$ under nitrogen (flow rate of 1 mL $min^{-1}$) using a Q500 thermogravimetric analyzer (TA Instruments, USA).

# 3. Results and discussion

All of the obtained xerogels were odorless fine white powders. The washed xerogels were insoluble in water, and only slight swelling occurred. In the case of the unwashed xerogels, the solid phase partly dissolved after the addition of water, which was most likely caused by the dissolution of low-molecular compounds (*i.e.*, potassium hydroxide, salts, short-chain polymers, *etc.*). The chemical compositions of the xerogels, as determined by XRF, are shown in Table 1.

As is evident from the data in Table 1, the potassium content significantly decreased after the washing step, and the Si/Al and K/Al molar ratios also changed markedly, which was caused by the dissolution of the low-molecule compounds. The Si/Al and K/Al molar ratios in the washed xerogel were close to the theoretical composition of poly(sialate-siloxo) [4]. After the hydrothermal treatment, the Al content slightly decreased and the molar ratios of Si/Al and K/Al slightly increased, which could be attributed to structural changes caused by the hydrothermal treatment.

FTIR spectra of the tested xerogel samples are depicted in Fig. 1. Software analysis of the FTIR spectrum of the unwashed xerogel sample indicated the presence of hydrogen carbonates (bands at 1400 and 830 $cm^{-1}$) and aluminosilicate compounds (bands at 1000 and 700 $cm^{-1}$). These findings are in agreement with the data presented by other authors [25-27]. The origin of the hydrogen carbonates in the unwashed xerogel can be sought in reactions of contained KOH with atmospheric $CO_2$. In the FTIR spectrum of the washed xerogel sample, the bands indicating the presence of hydrogen carbonates did not appear, evidently because the hydrogen carbonates were dissolved during the washing procedure. In the case of the samples treated under hydrothermal conditions, several new bands appeared. The obvious bands at 440 $cm^{-1}$ were identified as bending (Si,Al)–O vibrations, and the bands at 600 $cm^{-1}$ were identified as D4R or D6R (double 4- or 6-membered ring) vibrations. According to Rios and Williams [28], these bands are characteristic for

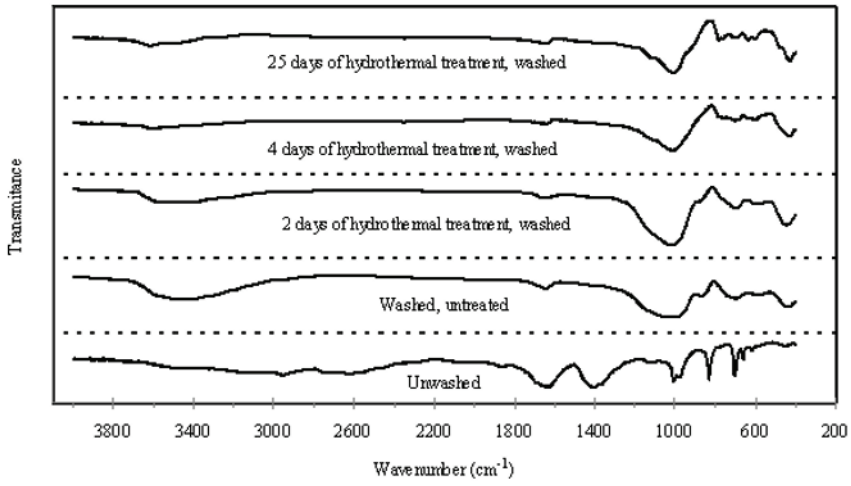


**Figure 1.** Comparison of the FTIR spectra of unwashed, washed and hydrothermally treated samples.

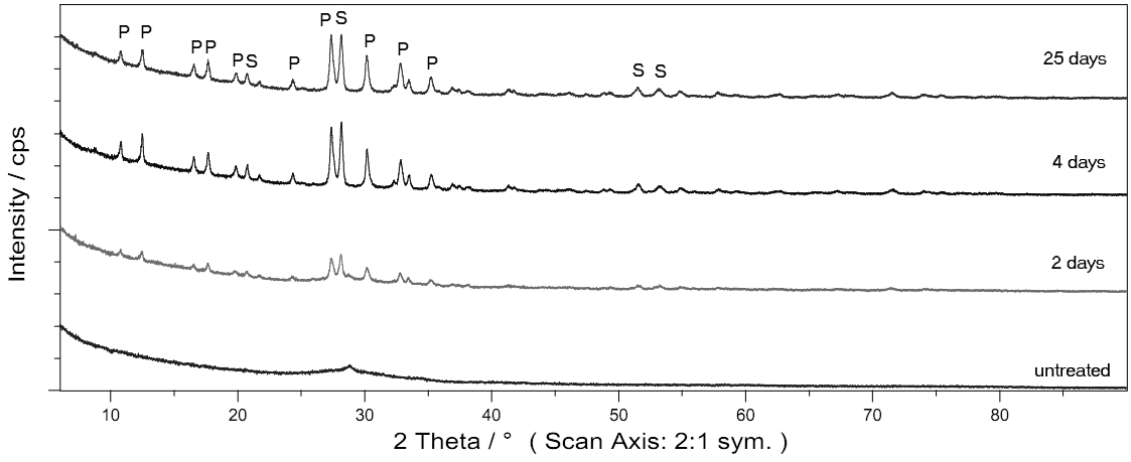


**Figure 2.** Comparison of the X-ray diffractograms of untreated and hydrothermally treated samples.

materials that contain zeolites, and they indicate that the transformation of the aluminosilicate polymer into zeolite under hydrothermal treatment most likely occurred. The software analysis of these spectra and a comparison with the database indicated the probable presence of phillipsite, a mineral of the zeolite group. The small band at 870 $cm^{-1}$, which was identified as an Al-OH vibration, gleaned interesting results. This band occurred in the untreated xerogel spectrum and within the spectra of the sample that was hydrothermally treated for 2 days. The absence of this band in the sample spectrum that was hydrothermally treated for 25 days indicates that the Al-OH functional groups contained in the aluminosilicate polymer were consumed by a chemical reaction during the hydrothermal treatment, most likely by continued condensation.

XRD results for the untreated washed xerogel and the xerogels that were washed after hydrothermal treatment are shown in Fig. 2. No significant peaks were observed in the XRD pattern of the untreated sample; the background line was only slightly increased as a consequence of the amorphous polymeric phase. According to Davidovits [29], such a pattern, with a broad diffuse halo in the range of 27–29° 2θ, is characteristic for geopolymers. As the duration of the hydrothermal treatment of the unwashed xerogel was increased, a gradual growth of the crystalline phase occurred. The xerogel which was washed before hydrothermal treatment showed no increase in crystallinity (the XRD pattern was identical with that of the untreated sample). The transformation of the amorphous aluminosilicate polymer into a crystalline structure most likely required an alkali environment. The main components of the crystalline phase formed in the hydrothermal treatment of the unwashed xerogel samples were identified as phillipsite (P) and silica/quartz (S). The occurrence of phillipsite has been described in the literature both during zeolite synthesis from coal combustion by-

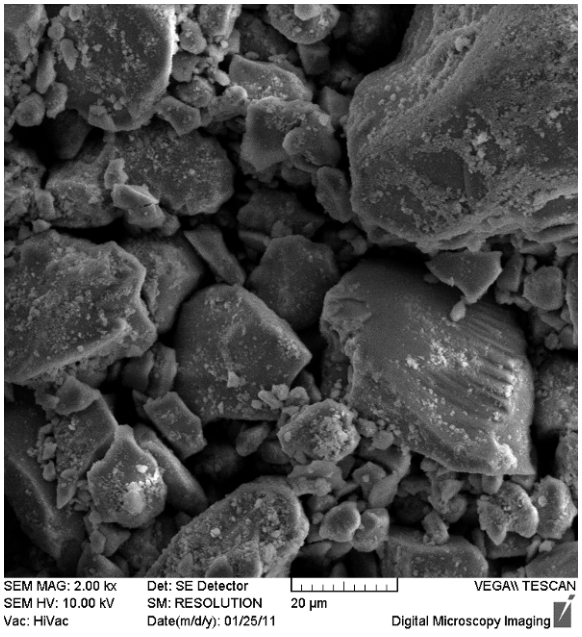


**Figure 3.** SEM image of an untreated sample.

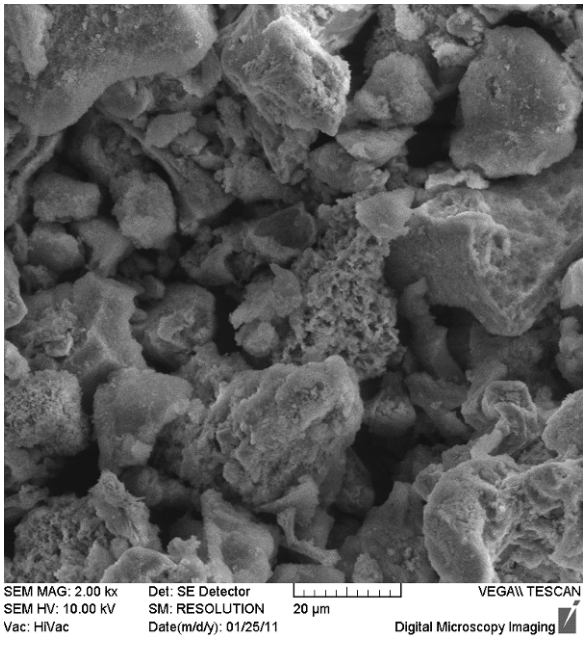


**Figure 4.** SEM image of a sample that was hydrothermally treated for 2 days.

products [28] and during geopolymer synthesis from fly ash [30]. The presence of phillipsite also concurred with the findings of Kolousek *et al*. [21], who synthesized phillipsite from kaolin using solutions of KOH or NaOH.

Changes in the morphology of the xerogel samples during the hydrothermal treatment were observed using SEM. No regular units indicating the presence of a

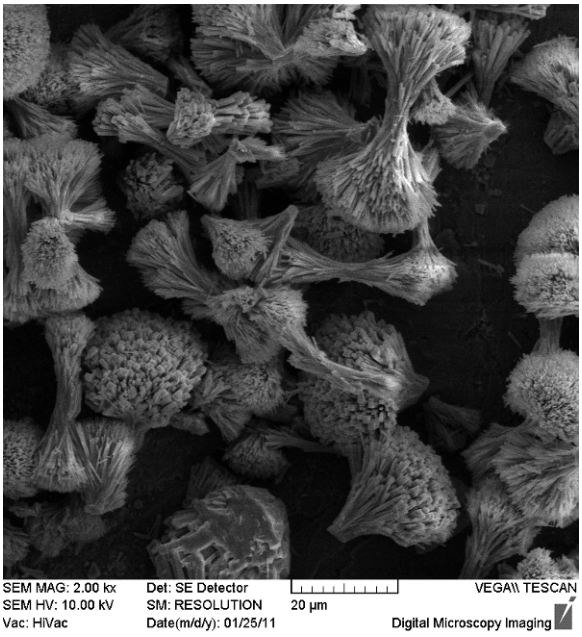


**Figure 5.** SEM image of a sample that was hydrothermally treated for 25 days.

crystalline phase were found in the washed untreated sample (Fig. 3), which is in agreement with the FTIR and XRD analyses. Some regular structures could already have been seen in the SEM image of the xerogel sample that was hydrothermally treated for two days (Fig. 4). As expected, obvious regular structures were observed in the sample treated under hydrothermal conditions for 25 days (Fig. 5). According to the SEM images, these structures appear to be identical with those of the natural phillipsite [31].

The changes in the properties of the xerogel samples during the hydrothermal treatment were also studied by thermogravimetric analysis (TGA). The comparison of TG/DTG curves of a hydrothermally treated sample (Fig. 6) and an untreated sample (Fig. 7) shows that the hydrothermally treated sample exhibited a maximum in the weight loss at a temperature of approximately 125°C, while the untreated sample had the greatest weight loss at 50°C. The course of the DTG curve of the hydrothermally treated sample is very similar to that of natural phillipsite reported by Garcia [32] and concurs with findings by Reeuwijk [33] that dehydration of phillipsite occurs at 120°C. The untreated sample did not exhibit such a sharp peak at 125°C in the differential thermogravimetric curve, however, its total weight loss was slightly higher. These results confirm changes in the structure of the aluminosilicate xerogel during hydrothermal treatment and formation of a crystalline phase indicated by another method described in this paper.

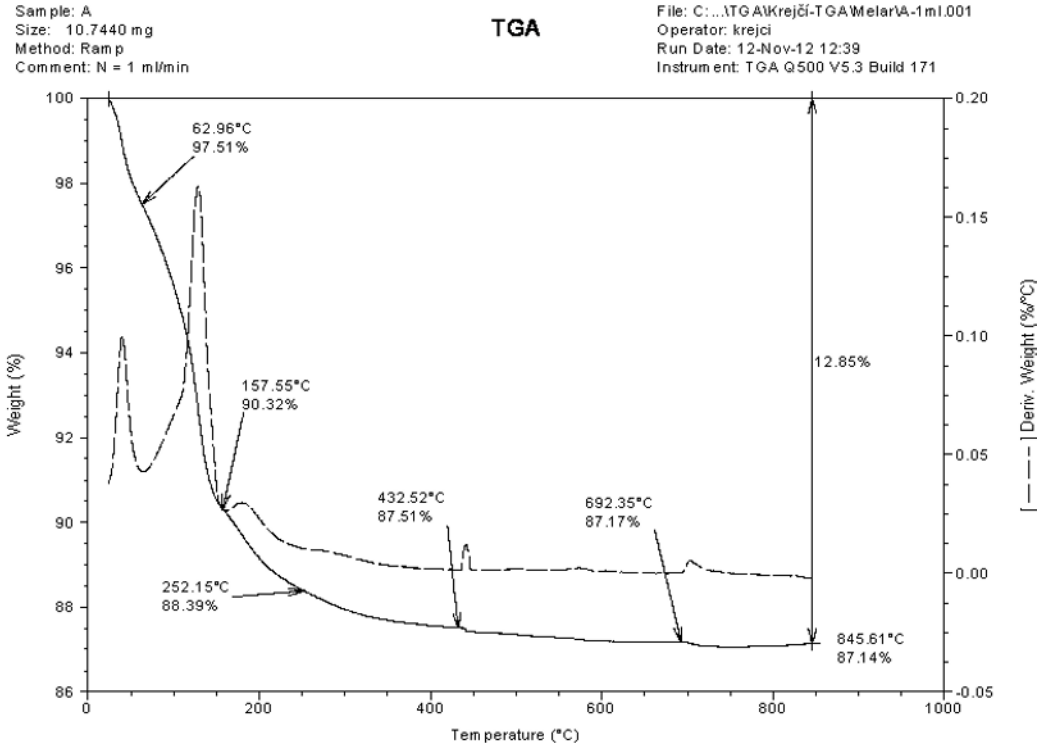


**Figure 6.** TG/DTG curve of a sample that was hydrothermally treated for 25 days.

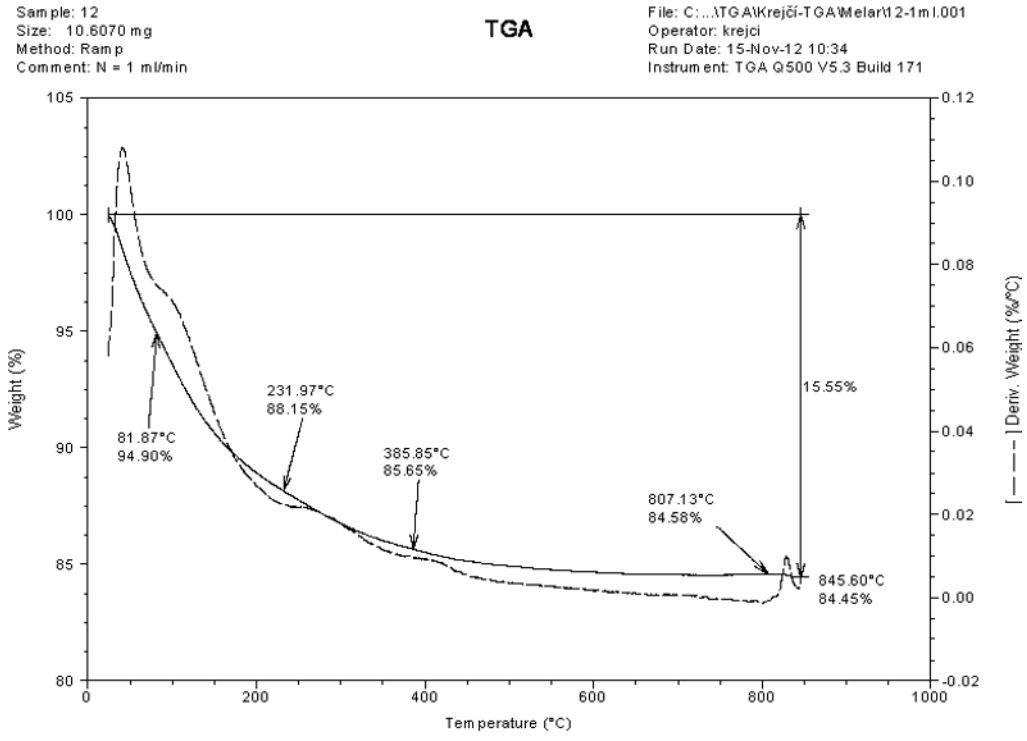


**Figure 7.** TG/DTG curve of an untreated sample.

## 4. Conclusions

XRD and FTIR analyses, along with SEM imaging and thermogravimetric measurements, confirmed that the structure of the aluminosilicate polymer prepared by the reaction between hydroxoaluminate and silicate in aqueous alkaline solution changes from amorphous to crystalline during hydrothermal treatment at 145°C in the presence of alkali hydroxide. According to the FTIR analysis, free Al-OH functional groups in the aluminosilicate polymer are consumed during the hydrothermal treatment, most likely by continued condensation. The formed crystalline phase has been identified as phillipsite, a mineral of the zeolite group.

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