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Production of mono-anorthite phase through mechanical activation

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Abstract

The structures of kaolinite, calcite and corundum were strongly deteriorated with activating the mixture with high energy planetary mono mill. Anorthite formation kinetics of activated and non-activated mixtures were studied by Differential Thermal Analysis under a heating rate of 5–30 °C, using Kissenger plots. The crystallization of anorthite showed an activation energy of 325 kJ mol^{-1} for mechanically activated and of 475 kJ mol^{-1} for non-activated samples. Both specimens crystallized by bulk nucleation. The phase formations were investigated upon heating at 1000–1100–1200–1300 °C. The structure of anorthite, for activated samples, was almost restored after firing at a temperature as low as 1100 °C for which the non-activated samples had to be fired at 1200 °C.

Keywords: Anorthite; Reaction kinetics; Mechanical activation; DTA; Rietveld refinement

1. Introduction

Anorthite ($CaAl_2Si_2O_8$) is one of the most important members of the plagioclase feldspar family [1], which are promising materials for substrate applications in electronics industry due to their good physical properties. Anorthite has a thermal expansion coefficient of $45 \times 10^{-7}\ K^{-1}$ and low dielectric constant of ~6.2 at 1 MHz. This is reasonably a good match to silicon [2,3]. Because of these desirable properties, anorthite ceramics have attracted attention and several studies have been carried out in order to decrease the sintering and crystallization temperature below 1000 °C [4–7].

According to the $CaO–Al_2O_3–SiO_2$ phase diagram, pure anorthite has a melting point of 1553 °C [8], which makes the solid-state synthesis of pure anorthite quite difficult at relatively low temperatures. In the last decade, it has been a challenge to decrease the firing and crystallization temperature via adding sintering agents such as B_2O_3, Na_2O and MgO [9,10]. On the other hand, anorthite ceramics are applied in tableware with a low relative refractive index between anorthite crystals and glassy phase, which improves its service performance. Taskiran et al. [11] studied the influence of mixing/milling on sintering behavior and technological properties of anorthite based stoneware. They concluded that it was possible to obtain a minimum amount of closed porosity in the microstructure, which increased the flexural strength to 110 MPa after 48 h mixing/milling. Taskiran et al. [12] designed a new material from a mixture of wollastonite, alumina, quartz, magnesia, and ball clay. In the material, which exhibited a high degree of whiteness and high strength, anorthite was found to be the major phase, and corundum, cristobalite, and glass appeared as minor phases after sintering at 1200–1230 °C for 3 h. Ustundag et al. [13] investigated the effect of slip solid content and sintering temperature on the

Table 1
X-ray quantitative mineralogy and particle size analysis of Yaylayolu kaolin [15].

Mineralogy (wt%)				
Kaolinite	Illite	Quartz	Rutile	Alunite
95.5–99.3	0.0–0.9	0.5–1.6	0.0–1.3	0.0–2.4
Particle size distribution (%)				
≤2 μm	−5, +2 μm	−10, +5 μm		−45, +10 μm
84.24–91.15	11.20–14.28	0.00–1.48		0.00

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Table 2
XRF analysis of raw materials (wt%).

	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2	SO_3	LOI	Total
Kaoline [15]	46.831	36.818	0.843	0.053	0.338	0.293	0.878	0.095	0.275	13.578	100
Corundum	0.133	99.41	0.052	–	0.083	0.222	–	–	–	–	100
Calcite	0.087	0.053	0.043	0.418	73.594	–	0.295	–	0.003	25.506	100

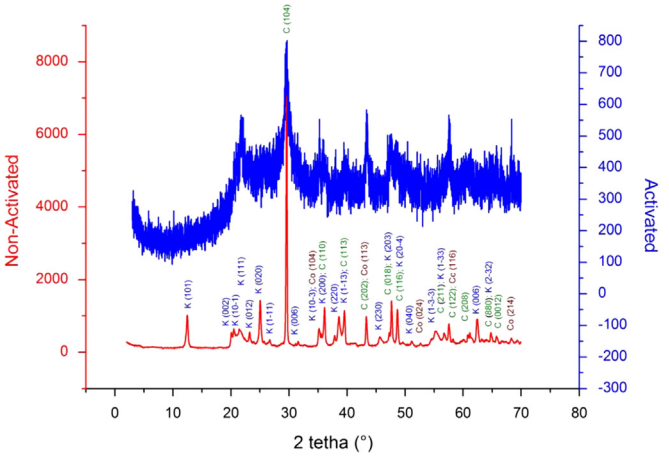

Fig. 1. XRD pattern of activated and non-activated raw samples K: kaolinite, C: calcite, Co: corundum.

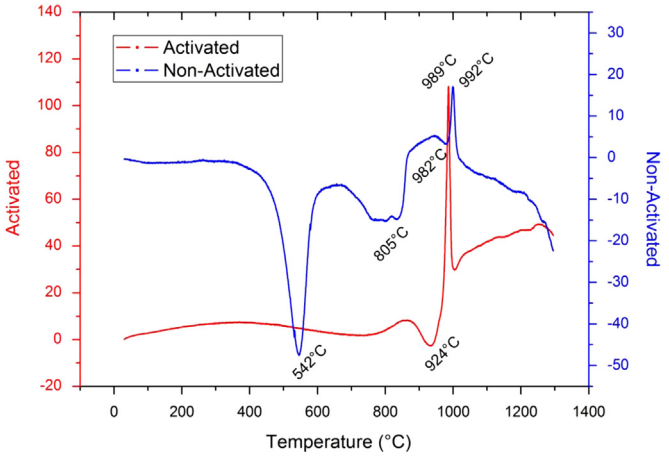

Fig. 2. DTA curves at 10 °C min^{-1}.

mechanical behavior of whiteware body by using mostly non-plastic pre-fired materials. They concluded that porosity of the materials reached a minimum at 45 vol% slip content and 1350 °C was the optimum sintering temperature at which a maximum flexural strength of 135 MPa was obtained [13]. Most recently, Cheng et al. [14] designed a single crystalline phase on anorthite. They used 20 wt% of ball clay, 20 wt% of quartz, 30 wt% of calcite and variable amount of feldspar and alumina in order to improve densification. They found out that 1230 °C was the optimum sintering temperature at which the flexural strength was 103 MPa. Single phase anorthite had a high degree of whiteness (L*94) and excellent translucency with an 87% of theoretical density. The relatively low

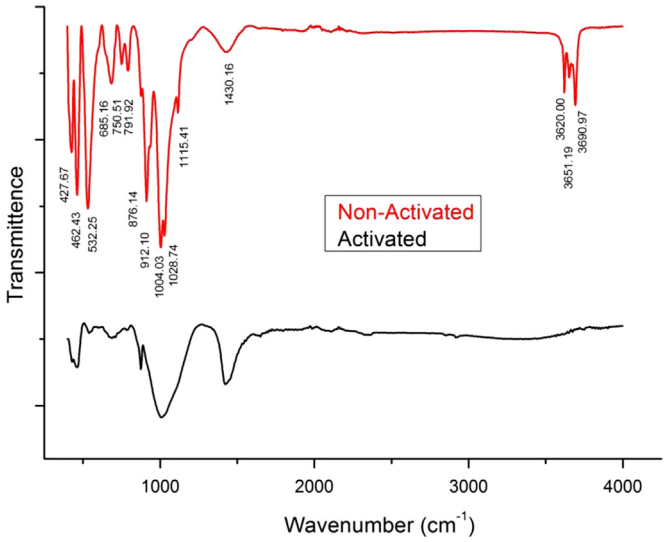

Fig. 3. FTIR spectra of the samples.

(4.9×10^{-6} K^{-1}) thermal expansion coefficient was stated to be a good match with the glaze.

In this study, anorthite was synthesized by using the raw materials both through the conventional techniques and by employing mechanical activation. The effect of mechanical activation on the anorthite crystallization kinetics was determined by the Kissenger method and the crystal structure parameters were studied in details by Rietveld refinement.

2. Material and method

Yaylayolu Kaolin (Kutahya, Turkey), industrial calcite and alumina were used as raw materials for anorthite synthesis. The detailed characterization of the Yaylayolu kaolin was studied by Yanik [15]. The mineralogical and particle size analysis of the Yaylayolu Kaolin are given in Table 1. The chemical properties of raw materials were determined by X-ray fluorescence (PANanalytical, Axios) method and are listed in Table 2. Powder mixture was prepared in stoichiometric proportions to obtain 1:1:2 anorthite ($CaO:Al_2O_3:2SiO_2$) composition. A typical recipe, which consists of 70 w% kaolin, 27.5 w% calcite and 2.5 w% corundum stoichiometric powders, were ball milled for 6 h with alumina balls and water. Half of the non-activated stoichiometric mixtures were mechanically activated in a high energy planetary mono mill (Fritsch Pulverisette 7). For 10 g of mixture, 100 g of zirconia balls were used as the grinding media in a 250 ml tungsten carbide mill container. Grinding time and grinding rotational