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Effect of annealing conditions on the structure, phase and granulometry composition, and reflectance spectra and their changes on irradiation for calcium silicate powders

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HIGHLIGHTS

- High temperature annealing of calcium silicates.
- Synthetic wollastonite produced from multicomponent system.
- High-temperature phases of pseudo-wollastonite and silica.

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ABSTRACT

High-temperature annealing of hydrated forms of calcium silicate produced in the multicomponent system $CaCl_2$–Na_2SiO_3–H_2O yields the formation of a heterophase structure containing high-temperature phases of pseudo-wollastonite and silica. Under these conditions, it is observed that there is an increase in the calcium silicate crystal lattice energy, particle size, reflection coefficient in the visible and near-IR spectral ranges, and radiation stability of the synthesized powders. The improved characters make the work useful, interesting and important.

1. Introduction

Natural silicates and their synthetic analogues are known to be used in the manufacture of construction materials, ceramics, glasses, and various coatings along with other fields of industry. One of the promising directions of advanced research consists of examining the possibility of producing silicate-based pigments of different composition and structure [1–3]. In view of the statements above, calcium silicates, in particular wollastonite ($Ca_6Si_6O_{18}$), are of special interest. Calcium silicates of different compositions and structures have extensive applications in manufacturing, construction materials, paper, paints, plastics, composite, polymer, metal-ceramic materials, and sorbents for water treatment and purification. In some cases, they serve as high-quality replacement for talc, kaolin, chalk, and titania. A broad range of applications of calcium silicates in different fields is related to their valuable physical-chemical and technological properties.

Wollastonite is an interesting, but not yet thoroughly studied

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material. The practical importance and perspectives of the wollastonite raw materials were properly evaluated for the first time in USA, and for already more than 50 years, the research on wollastonite properties and the development of new materials on its basis are rather being continuously carried out globally [4]. At present, wollastonite is one of the promising mineral fillers applied in different industries as an additive to materials to increase their strength and thermal resistance, to improve their dielectric and electrical characteristics and to decrease the duration of technological processes in course of manufacture and the processing temperature [5,6]. One of the promising and interesting fields for application of the synthetic wollastonite is its application in production of pigments for lacquers, paints, and other types of coatings [7,8]. Studies of the processes of pigment production using wollastonite are underway in Russia. Sedel'nikova and Pogrebenkov and Sedel'nikova et al. [9,10] investigated the production of ceramic pigments using natural wollastonite. Bikbau and Kuz'mina [11] explored the method for producing the pigment for paints and enamels by employing titania pigment and wollastonite (up to 30%) and according to the suggested method, the pigment whiteness obtained was 91.6–97%. Application of calcium silicates allows for a reduction in the pigment cost due to titania savings. Ziganshina and Usmanova [12] described the properties of modified manganese pigments for decorative polymeric composites and produce manganite-silicate and calcium manganite pigment, after modification with calcium silicate.

United State (USA),China, and India are most significant global manufacturers and consumers of wollastonite [13–15]. Availability of naturally occurring wollastonite is relatively less: annual production of 0.5–0.7 million MT worldwide [16]. In Russia, there are a number of known wollastonite deposits in Siberia, Ural, and Karelia. However, inspite of high demand, its production is virtually negligible [4,6]. Due to gradual increase in demand for wollastonite and remoteness of the production sites from the customers, a substantial interest is concerned with the application of synthetic wollastonite. Valuable properties have been imparted to wollastonite through addition of various materials in synthetic wollastonite in the manufacturing units in Great Britain, France, Germany, USA, Italy, and Denmark [16–17].

In another study, we investigated optical properties of calcium silicates synthesized in the $CaCl_2$–Na_2SiO_3–H_2O system and demonstrated their applicability in production of composite materials based on polyvinyl chloride [18,19]. It was observed that calcium silicates obtained in the system possessed a high reflection coefficient at wavelengths of up to 200 nm. Whiteness of the samples under study was calculated from the diffuse reflectance spectra and was equal to 95–98%. In present work, the effect of thermal treatment conditions on the structure, phase and granulometric compositions, and diffuse reflectance spectra and their changes upon irradiation by accelerated electrons on as-synthesized wollastonite produced by using $CaCl_2$–Na_2SiO_3–H_2O system were investigated.

2. Experimental

2.1. Synthesis of calcium hydrosilicate and wollastonite

The components for the synthesis of calcium hydrosilicate, solutions of sodium silicate with a silicon content of 22.4% (silicate unit $SiO_2/Na_2O = 1$) and calcium chloride with the $CaCl_2 \cdot 2H_2O$ content of at least 98.3% were mixed in an aqueous medium in open vessels [20]. The obtained white precipitate was thoroughly washed until the complete removal of Cl^- ions, whose presence was controlled by the reaction of the washing fluid with an $AgNO_3$ solution, filtered through a 'Whatman Grade 42' filter paper, and dried at 85 °C. To produce the crystalline precipitates (wollastoite and pseudo-wollastonite), calcium hydrosilicate was annealed in an SNOL 6.7/1300 muffle furnace in the temperature range of 850–1100 °C for 2 h and at 1200 °C for 2, 3, and 5 h.

2.2. Methods of analysis

Carbonates contained in the obtained sample of calcium hydrosilicate (calculated using – the dry sample) were quantitatively determined by the gas-volumetric method based on measuring the volume of gas emitted from the solid sample [21].

X-ray diffraction patterns of precipitates were registered using a D8 ADVANCE automatic diffractometer with the sample rotation in the CuK_α-radiation. The X-ray diffraction analysis was performed using the EVA search program and the PDF-2 powder database.

The samples' specific surface area was determined by the method of low-temperature nitrogen adsorption using a Sorbtometer-M device.

The samples IR-spectra were registered in the range 400–2000 cm^{-1} using a Shimadzu FTIR Prestige-21 Fourier spectrometer at room temperature. Prior to registration, the samples were ground in an agate mortar until in a finely dispersed state and then deposited on a substrate made of the KRS-5 glass in the form of suspension in Vaseline oil.

Analysis of the particle size distribution in the obtained calcium silicates was carried out using an ANALYSETTE 22 NanoTec particle size laser analyzer (FRITSCH, Germany).

Studies of diffusion reflectance spectra (ρ_λ) and powder irradiation with electrons ($E = 30$ keV, $\Phi = 2 \times 10^{16}$ cm^{-2}, $T = 300$ K, and $P = 5 \times 10^{-7}$ torr) were carried out in a "Spektr" simulator of outer space conditions [22]. The ρ_λ spectra were registered in vacuum on the site of powders irradiation (*in situ*). This method avoids an interaction created by radiation defects with atmospheric oxygen. In the atmosphere, the concentration of such defects is reduced as compared to a vacuum. Therefore, when measurements in the atmosphere were made, it lowers their concentration.

3. Results and discussion

XRD of the synthesized wollastonite (Fig. 1) was carried out to know the presence of various species in it. The figure shows diffractograms of the initial synthesized sample and those upon annealing at different temperatures. As seen from the above figures, the as-synthesized calcium silicate is X-ray-amorphous. However, the sample was found to contain crystalline phases of calcium carbonate in the form of calcite and aragonite. The main factor responsible for $CaCO_3$ formation is related to the carbonization of calcium hydroxide that was formed during interaction of the amorphous calcium silicate with water and the carbon dioxide dissolved in it. The amount of $CaCO_3$ was determined and was found to be 30% [22]. The synthesized sample thus comprised of both calcium silicate as well as calcium carbonate along with amorphous silica.

Upon annealing in given temperature range, the given X-ray diffraction patterns revealed major characteristic peaks corresponding to the crystalline phase of the wollastonite of the triclinic modification (PDF-2, 01-076-0186) with the following unit cell parameters: a–7.94; b–7.32; ≳–7.07; $\alpha = 90.03$; $\beta = 95.37$; and $\gamma = 103.43$. Annealing at 1200 °C yielded the formation of the high-temperature modification of wollastonite in the form of phases of pseudo-wollastonite of the monoclinic modification, but with different crystal unit cell parameters (PDF-2, 01-089-6463: a–11.83; b–6.86; ≳–10.52; $\alpha = 90.00$; $\beta = 111.24$; $\gamma = 90.00$ and PDF-2, 01-089-6485: a–6.83; b–11.87; ≳–19.63; $\alpha = 90.00$; $\beta = 90.66$; and $\gamma = 90.00$). Moreover, upon annealing at 1200 °C,