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Influence of mechanical activation on sphene based ceramic material synthesis

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Abstract

Sphene ($CaTiSiO_5$), a calcium titanosilicate ceramic has been prepared from a powder mixture of $CaCO_3$, TiO_2 and SiO_2 using vibro-milling for homogenization and activation of precursors. The mechanochemical process initially yielded amorphous powders, which on further calcination, crystallized to yield sphene ceramic. The evolution of the phase composition with thermal treatment was investigated by X-ray powder diffraction (XRPD). Powder morphology and particle size distribution were analyzed by scanning electron microscopy (SEM) and laser diffraction, respectively. Rietveld refinement was employed to get the structural information of the synthesized powder. Densification and microstructure evolution was determined by means of density and scanning electron microscopy (SEM). The most favorable conditions for mechanical activation and synthesis of sphene based ceramic material are reported.

Keywords: Sphene; Mechanochemistry; Rietveld refinement; SEM/EDS

1. Introduction

Sphene or titanite is a nesosilicate mineral with monoclinic symmetry. It can crystallize both as primary (space group $A2/a$) and lower-T phase (space group $P2_1/a$). The ideal chemical formula of sphene can be written as $CaTiSiO_5$ or $CaTiO(SiO_4)$ [1]. However, within the structure, significant substitutions in both cation and anion sites may occur. Calcium, in coordination 7, can be replaced with Mn [2], then Sr, Ba, rare earth elements and Th when high valence is compensated by joining Fe^{3+} and Al by Ti [3]. Titanium, in coordination 6, can be replaced with Al^{3+} [4], Fe^{3+} [5], Ta [6] and Nb [7,8] compensating the charge difference by incorporating Na instead of Ca. Dual substitution of Fe and Al with Ti and OH, Cl, F, with O, are only possible in natural sphene [9,10]. Ribbe [11] noted that all Ti atoms are moved out from their geometric center in octahedrons in the same direction along the axis a, which is reflected in structure geometry i.e. longer and shorter Ti–O bonds.

Because of the distorted TiO_6 octahedra and consequent low point symmetry, titanite is desirable to develop an intense coloration [12]. Ones that contain Cr^{3+} are used as pink pigment for painting ceramics in pink and purple [13]. Furthermore, titanite also has a good thermal stability and it is an excellent candidate for a host lattice of ceramic materials [14]. It can also be used for nuclear waste disposal [15–17] or luminescent materials [18], since it is possible to incorporate a variety of elements into its crystal lattice. In high concentrations sphene is a potential source of titanium [19].

It is very difficult to obtain pure synthetic monophase titanite. Many different methods such as: sol–gel [20], coprecipitation [20], combustion [21], spray pyrolysis [22], freeze-drying [23] and hydrothermal methods have been used. In most cases pure sphene was not obtained. There are always some traces of crystobalite (SiO_2), perovskite ($CaTiO_3$), wollastonite ($CaSiO_3$) and other phases, besides sphene.

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The aim of this work is to explore the influence of mechanochemical activation of precursors prior to synthesis of sphene. Publications cover mostly grinding of natural sphene concentrates [24,25]. Mechanochemistry represents an alternative route in synthesis of sphene. So far, many materials are synthesized by this method in the form of nanoparticles and nanocrystalline powders [26]. In this study, vibratory mills are used. They are classed with grinding devices operating via impact and attrition. In such mills the impact is produced by the grinding body sliding over the material being ground or rotating around some axis. Mechanochemical routes are attractive because of their simplicity, flexibility, and ability to prepare materials by solid state reactions at room temperature [27]. Finally, it is simpler and easier to implement this method in industrial level.

2. Experimental methods

2.1. Powder preparation

Reactants used in the synthesis are commercially obtained powders: TiO_2 (Lab. Art. 808E. Merck), SiO_2 (ASP-K-amorphous, Prahovo) and $CaCO_3$ (pro analysi, 11490, Kemika, Zagreb). All precursors have been dried at 105 °C for 24 h and stored in an exsicator to avoid atmospheric moisture before weighing. Four samples were prepared from stoichiometric amounts of these powders in order to obtain 5 g of sphene (2.5529 g TiO_2, 2.0344 g SiO_2, 1.5324 g $CaCO_3$). The powder mixtures were homogenized in the vibratory mill (Fritsch Pulverisette Analysette Laborette, type 09 003, no. 155, 380 V). The Vibratory Pulverizer uses ring ($ø=5.3$ cm, $h=4.3$ cm) and a disk ($ø=10.3$ cm, $h=4.3$ cm) inside a hard-metal tungsten carbide grinding bowl ($ø=13$ cm, $h=6.3$ cm). Volume of the container is 100 ml with $m=3200$ g. The device can operate at two speeds of vibration: 750 min^{-1} and 1000 min^{-1}. Samples were ground up to 2 h in air atmosphere (15 min, 30 min, 1 h and 2 h) with speed of 750 min^{-1}.

Five pellets were made from each sample for different grinding time ($ø=8$ mm, $h=5$ mm). They were obtained by hydraulic pre-pressing under the pressure of 100 MPa. Sintering of compacted powders was carried out at different temperatures (from 900 to 1300 °C) in air at a heating rate of 10 °C/min and a soaking period of 2 h in alumina crucibles.

2.2. Characterization

Before any calcinations, the average particle size and particle size distribution were determined by particle size analyzer (PSA) using Mastersizer 2000 (Malvern Instruments Ltd., UK). Particle size analyzer, based on laser diffraction, covers the particle size range of 0.02–2000 μm. For the PSA measurements, the powders were dispersed in distilled water, in an ultrasonic bath (low-intensity ultrasound, at a frequency of 40 kHz and power of 50 W), for 5 min.

The sintered pellets were polished and thermally etched at temperature of 1150 °C for 30 min. Microstructure and chemical composition were investigated with Au/Pd coating using a scanning electron microscope (SEM) Vega TS 5130 MM, Tescan, coupled by EDS (INCA PentaFET-x3, Oxford Instruments).

Determination of the melting point of sintered sphene was followed by hot-stage microscopy (HSM) using Carl Zeiss-Jena termomicroscop with PtPt-Rh termocouple in range of 20–1350 °C.

All of the powders were characterized at room temperature by X-ray powder diffraction (XRPD) using Siemens D-500 diffractometer. Cu $K_{\alpha 1,2}$ radiation was used in conjunction with a Cu K_{β} nickel filter. The range of 10–90°2θ was used for all powders with a scanning step size of 0.02°.

Data for structural refinement were taken in the 2θ range 10–90°2θ, with the step of 0.02° and scanning time of 12 s per step. The refinement was performed with the FullProf computer program which adopts the Rietveld calculation method. The TCH pseudo-Voigt profile function was used.

3. Results and discussion

It is well known that grinding has a significant place in the processing of ceramic materials. It leads to physical and chemical changes in materials and in that case, grinding is referred to as mechanochemical treatment [28]. Mechanically induced violation of the mineral grain structure is accompanied by reduction of the size of the mineral particles and the associated increase in the specific surface area, accumulation of free energy on the particles and, thereby, by enhancement of the chemical activity of the surface layer [29].

In the volumetric size distribution (Fig. 1), sample with grinding time of 1 h shows the best uniformity, next is sample with grinding time of 30 min, then with 2 h grinding and in the end the one with 15 min of grinding.

Theoretical density was calculated for each sample after sintering. It was shown that the highest density have samples with grinding time of 30 min on 1200 °C and 1250 °C (Table 1). With the sintering temperature of 1200 °C the density is 3.33 g/cm^3 which represents ~95% of the theoretical value.

Sintering above 1300 °C leads to melting of the material (Fig. 2). Due to results from PSA and calculated density, sample with grinding time of 30 min was chosen for further analyses.

The microstructure of the sphene with grinding time 30 min heated at 1200 °C is shown in Fig. 3(a–d). The analysis shows bimodal grain structure that is in good agreement with volumetric size distribution analysis. The average particle sizes estimated from SEM images are 3 and 5 μm. The micrographs revealed the dense nature of the compact sintered at 1200 °C with the irregular shaped and elongated grains. Vibratory mills are very efficient as