



Synthesis of zirconium and hafnium germanates from mechanically activated oxides

V. Prokip^a, A. Utkin^{a,*}, N. Baklanova^a, A. Cherkov^b, B. Zaitsev^c, A. Mikheev^d

^a*Institute of Solid State Chemistry and Mechanochemistry SB RAS, 18 Kutateladze street, Novosibirsk 630128, Russia*

^b*Novosibirsk State University, 2 Pirogova street, Novosibirsk 630090, Russia*

^c*SRC VB "VECTOR", Koltsovo, Novosibirsk region 630559, Russia*

^d*Nikolaev Institute of Inorganic Chemistry SB RAS, 3 Acad. Lavrentiev Ave., Novosibirsk 630090, Russia*

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Abstract

The peculiarities of the synthesis of zirconium and hafnium germanates ($ZrGeO_4$ and $HfGeO_4$) from mechanically activated oxides (GeO_2 , ZrO_2 and HfO_2) have been studied. The phase, structural and morphological evolutions of the products obtained by thermal treatment of mechanically activated oxides were studied by a set of analytical techniques. The results showed a significant decrease in GeO_2 crystallite size during mechanical treatment, whereas the size of HfO_2 and ZrO_2 changes only slightly. Mechanical treatment of mixtures results in great change of morphology, an increase in particles contact area and partial amorphization of GeO_2 . Mechanical activation promotes a significant reduction of the temperature of compound formation, reaction rate and yield. Possible mechanisms of activation effect are discussed.

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1. Introduction

Hafnia and zirconia-based refractory ceramics, including hafnium and zirconium germanates, are of both scientific and technological interest as structural and functional materials due to a number of promising properties. Hafnium and zirconium germanates ($MGeO_4$, $M = Hf, Zr$) have a layered sheelite-like ($CaWO_4$) structure [1,2], high resistance to chemical attack by strong acids and alkalis, stability in oxidizing environments and thermal stability up to 1800 °C [3,4]. These properties allow us to consider these compounds as promising candidates for the heat resistant–high strength structural ceramic materials or protective coatings for the high-temperature structural applications [5,6]. The most significant prospective property of $HfGeO_4$ and $ZrGeO_4$ is the UV/visible fluorescence emission under X-ray radiation, which makes them promising X-ray scintillators [7,8]. It was shown that scintillating properties of germanates are greatly dependent on

their phase composition. For example, X-ray/UV conversion was observed for $HfGeO_4$ of only stoichiometric composition but not for $Hf_{1-x}Ge_{1+x}O_4$ solid solutions [8].

Previously, three approaches have been proposed for the synthesis of hafnium and zirconium germanates [1,2,8–11]. The first of them is a co-precipitation route, which allows obtaining single-phase germanates at a relatively low temperature (1000–1100 °C) [9,11]. However, this method involves multiple stages and the use of a set of reagents, which makes this route unsuitable for some applications. Besides, germanates obtained by this route demonstrated weak fluorescence properties, which could be due to impurities or the residual OH-groups.

The other route is hydrothermal synthesis [8]. It was found that the hydrothermal crystallization resulted in well individualized nanoparticles with no X/UV conversion properties. The thorough analysis of the reasons of this behavior suggested that germanium was partially solubilized from the amorphous precursor under hydrothermal conditions, resulting in the crystallization of germanium-deficient hafnium germanate possessing no X/UV conversion properties.

*Corresponding author: Tel.: +7 383 233 24 10.

E-mail address: utkinalex@hotmail.com (A. Utkin).

The solid-state route that implies the direct interaction of zirconium or hafnium oxide with germanium oxide is very attractive due to its simplicity in terms of both the synthesis procedure and the reagents [1,2,10,11]. The major drawback of this route is the high temperature of synthesis (1300 °C) resulting in slow volatilization of GeO₂ followed by the shift of the stoichiometry of solid products and the change of their phase composition [1,2,10]. The loss of GeO₂ and low reaction rate result in difficulty in obtaining single-phase germanates by this approach. To overcome this disadvantage, the solid-state synthesis of germanates was recommended to be conducted under the high GeO₂ vapor pressure conditions [1,2] which, in its turn, requires special experimental equipment. A decrease in the synthesis temperature is not desirable because of very slow reaction rate at temperatures lower than the melting point of GeO₂. Thus, a search of the appropriate chemical route(s) for obtaining stoichiometric zirconium and hafnium germanates is permanent issue.

It is well known that the mechanical activation of reagents can be used to accelerate reactions between solids [12]. Mechanical activation involves high-energy collisions of the milling media and reactant powders, resulting in pulverization, phase transformation and chemical reactions during intensive ball milling [13]. There is a great number of literatures concerning the favorable effect of preliminary mechanical treatment on the acceleration of the interaction of solids including solid oxides (see, e.g. [13] and refs therein). However, no data concerning the usage of mechanical activation for the synthesis of hafnium and zirconium germanates were found.

The aim of this work was to study the effect of preliminary mechanical treatment on the interaction of zirconium (or hafnium) oxide and germanium oxide at elevated temperatures.

2. Experimental

2.1. Initial substances

Hexagonal GeO₂ (electronic grade, 97% purity (2.5% H₂O, 0.5% Cl), JSC Germanium, Russia), monoclinic ZrO₂ (chemical grade, 99.9%, Reachim, Russia) and monoclinic HfO₂ (chemical grade, 99.9%, GICI, Ukraine) were used as zirconium and hafnium germanate precursors.

2.2. Mechanical treatment of oxides

Mechanical treatment was performed in a planetary ball mill PM 100 CM (Retsch, Germany) in air. The corresponding quantities of the initial ZrO₂, HfO₂ and GeO₂ powders, with MO₂:GeO₂ equimolar ratio (M=Zr or Hf) were mixed in a mill jar to obtain stoichiometric ZrGeO₄ and HfGeO₄ compounds. The sample milling was performed at a constant speed of 600 rpm with time ranging between 5 and 60 min. The mill jar and balls were made of yttria-stabilized zirconia (YSZ) and the balls/sample mass ratio was equal to approximately 5. Experimental conditions of high-energy ball milling of mixtures are listed in Table 1. For comparison, the initial oxides were separately milled for 60 min under the same experimental

conditions. Then, mechanically activated ZrO₂ and GeO₂, HfO₂ and GeO₂ powders were carefully mixed in agate mortar.

2.3. High-temperature treatment of oxide mixtures

The initial and mechanically activated powder mixtures were heated in air in the diffractometer chamber with a constant heating rate of 30 °C/min in the 25–1200 °C temperature range with sample exposure at 900, 1000, 1100, and 1200 °C. Dwell time at each temperature was 5 min. In addition, mechanically treated powder mixtures were calcined in the muffle furnace at 1200 °C with exposure to air for 6 h.

2.4. Characterization

The morphology and elemental composition of products were examined by S-3400N and TM-1000 (Hitachi, Japan) scanning electron microscopes coupled with OXFORD INCA Energy 200 (Oxford Instruments, UK) energy dispersive spectrometer and SwiftED-TM (Hitachi, Japan) software.

Transmission electron microscopy (TEM) micrographs were obtained with a high-resolution analytical transmission electron microscope JEM-2200FS (JEOL, Japan) with a resolution of 0.19 nm and accelerating voltage of 200 kV. Before observation, the aggregated powder was dispersed in ethanol by ultrasonic treatment for 5 min. After sedimentation of large-size fraction (dwell time 1–2 min.), a drop which contained a fine powder fraction was fixed on the grid.

The X-ray powder diffraction patterns of the initial oxides and products were recorded using D8 Advance (Bruker, Germany) diffractometer (Cu-K α radiation) equipped with high-temperature HTK-1200N (Anton Paar, Austria) chamber. The qualitative phase analysis was performed using the ICDD PDF-4 database (2008). The quantitative analysis including the refinement of cell parameters (accuracy: less than 0.1% of the measured values) and phase composition of products were carried out by the Rietveld method using the DIFFRAC^{plus} TOPAS software (Bruker, Germany) and ICSD data (1997).

Raman spectra were recorded using the RFS/100 spectrometer (Bruker, Germany) equipped with the Nd:YAG laser (1064 nm wavelength, 100 mW power). At least 200 scans were recorded for each sample. IR spectra were measured in the 550–5000 cm⁻¹ range with the resolution of 1 cm⁻¹ on Infracum FT 801 IR spectrometer (Simex, Russia) equipped with a microscope. The samples were prepared as pellets

Table 1
Experimental conditions of high-energy ball milling of the ZrO₂–GeO₂ and HfO₂–GeO₂ mixtures.

Atmosphere and pressure	Air, 1 atm
Jar's volume	50 cm ³
Total ball weight	32 g
Ball diameter	10 mm
Ball and jar material	Yttria stabilized zirconia (YSZ)
Mass charge	6.4 g
Acceleration	300 m/s ²

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