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Composition and microstructure of zirconium and hafnium germanates obtained by different chemical routes



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ABSTRACT

The phase composition and morphology of zirconium and hafnium germanates synthesized by ceramic and co-precipitation routes were studied. The products were characterized using high-temperature X-ray diffraction analysis (XRD), Raman spectroscopy, scanning electron microscopy (SEM) and thermal (TG/DTA) analysis. To investigate the phase composition and stoichiometry of compounds the unit cell parameters were refined by full-profile Rietveld XRD analysis. The morphology of products and its evolution during high-temperature treatment was examined by SEM analysis.

It was stated that there is the strong dependence of the phase composition and morphology of products on the preparation route. The ceramic route requires a multi-stage high-temperature treatment to obtain zirconium and hafnium germanates of 95% purity or more. Also, there are strong diffusion limitations to obtain hafnium germanate Hf_3GeO_8 by ceramic route. On the contrary, the co-precipitation route leads to the formation of nanocrystalline single phase germanates of stoichiometric composition at a relatively low temperatures (less than 1000 °C). The results of quantitative XRD analysis showed the hafnium germanates are stoichiometric compounds in contrast to zirconium germanates that form a set of solid solutions. This distinction may be related to the difference in the ion radii of Zr and Hf.

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1. Introduction

Germanates of IVB group metals are promising materials for different applications spreading from UV-emitting X-ray scintillators to high-temperature materials [1–4]. Thus, zirconium and hafnium germanates exhibit strong UV emission under X-ray excitation. This property together with high density of the compounds (6.0 g/cm³ for ZrGeO_4 and 8.5 g/cm³ for HfGeO_4) makes them very attractive for X-ray imaging and medical applications.

The other interesting and exciting application areas of germanates of IVB group metals arise from the peculiarities of their thermal behavior [5–7]. Thus, it was stated that the high-temperature decomposition of crystalline zirconium and hafnium germanates is accompanied by GeO_2 sublimation and the formation of sintered ZrO_2 or HfO_2 solid products [5]. Taking into attention that the decomposition of germanates is highly endothermic process and the resulting solid products have high melting points one can consider these germanates as candidates for thermal protection systems. On the contrary, decomposition of germanates of IVB group metals under special conditions results in highly porous oxides. Recently, Yang et al. reported that during decomposition of scheelite-type CeGeO_4 in ammonia atmosphere

the three-dimensional ceria foams with long-range and atomically thin single-crystalline walls can be derived [7]. Such ceria porous architectures are very attractive for catalytic or photovoltaic applications.

It is widely recognized that the functional properties of materials strongly depend on their composition and microstructure. This is especially true for zirconium and hafnium germanates. Actually, Hochepeid and co-workers [4] found that hafnium germanate (HfGeO_4), which was crystallized from different routes exhibits different UV/X-ray conversion properties, namely, HfGeO_4 , the composition of which was only slightly varied from stoichiometric, possessed no UV/X-ray conversion properties in contrast to strongly stoichiometric compound. This suggests that zirconium and hafnium germanates derived from different chemical routes need to be carefully characterized in terms of their structure, phase composition, morphology by various modern analytical techniques before they can be reliably introduced into devices, screens, thermal protection systems, etc.

One can note that the data on $\text{Zr}(\text{Hf})\text{O}_2\text{--GeO}_2$ systems are not complete and sometimes contradictory [8–11]. In the first time, zirconium and hafnium germanates were investigated by Lefèvre and Collongues in 1960s [8,9]. They synthesized sheelite-like $M\text{GeO}_4$ and $M_3\text{GeO}_8$ ($M=\text{Zr, Hf}$) germanates by solid-state and precipitation techniques and determined crystal structure parameters of the compounds. They found that the ZrGeO_4 - and Zr_3GeO_8 -based solid solutions are formed. Later, Colomban et al.

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[10] also reported about the formation of t -ZrO₂, Zr₃GeO₈ and ZrGeO₄-based solid solutions; however, their data differed from those presented by Lefèvre et al. [8,9]. As to the HfO₂–GeO₂ system, literature data on the formation of solid solutions are unknown.

The aim of this work was (i) to synthesize M GeO₄ and M_3 GeO₈ (M =Zr, Hf) germanates by two different chemical routes; (ii) to characterize and compare zirconium and hafnium germanates in terms of the phase composition, stoichiometry, and microstructure.

2. Experimental

2.1. Materials

As initial substances, m -ZrO₂, ZrOCl₂·8H₂O (chemical grade, 99.9%, Reachim, Russia), m -HfO₂ (chemical grade, 99.9%, GICI, Ukraine), HfCl₄ (chemical grade, 99.9% purity, Dalchem Ltd., Russia) and h -GeO₂ (electronic grade, 97% purity (2.5% H₂O, 0.5% Cl), “Germanium” Ltd., Russia) were used as germanate precursors. The initial HfCl₄ was hydrolyzed in 1 M HCl solution and slowly dried at the temperature of 80 °C to obtain the soluble HfOCl₂·8H₂O. Concentrated ammonia solution (99.99%, JSC “Chemicals”, Russia) was used for precipitation. Besides HfCl₄, all chemicals were used as-received without further purification.

2.2. Synthesis

Zirconium and hafnium germanates were synthesized by two different techniques. The first of them was so-called ceramic route and involves the heat-treatment of mixture of as-received oxides. The other approach was co-precipitation one.

To obtain Me GeO₄ or Me_3 GeO₈ (Me =Zr or Hf) phases, the corresponding quantities of monoclinic zirconium (hafnium) and germanium oxides (h -GeO₂) were thoroughly mixed in agate mortar and transferred to corundum crucible. The mixtures were heated with velocity of 5°/h till 1300 °C in air and kept at this temperature for 6 h. In some runs, exposition time was increased to 40 h with intermediate stops to homogenize mixture.

According to the second approach, the appropriate amounts of ZrOCl₂·8H₂O or HfOCl₂·8H₂O were dissolved in de-ionized water to form 1 mol/l solutions. Germanium dioxide was mixed with de-ionized water with following drop-by-drop addition of concentrated ammonia solution under continuous stirring to obtain 0.1 M solution. The addition of ammonia was stopped when all GeO₂ was dissolved. The appropriate volumes of as-prepared solutions were mixed under continuous stirring to obtain the Me GeO₄ or Me_3 GeO₄ precursors. 50 ml of concentrated ammonia was added to 100 ml of mixture to complete the precipitation process. The obtained gel was filtered and washed by concentrated ammonia solution to minimize the content of chlorine in precipitates. The obtained precipitates were dried on air forming transparent glass-like xerogels. Xerogels were calcinated on air at 1000 °C during 1 h. The products were white powders.

2.3. Sample characterization

The morphology and elemental composition of products were examined by the scanning electron microscopy (SEM) using MIRA3 TESCAN and TM-1000 (Hitachi Ltd., Japan) microscopes coupled with energy dispersive spectroscopy (EDS) using OXFORD INCA Energy 200 (Oxford Instruments Ltd., GB) and SwiftED-TM (Hitachi Ltd., Japan). The X-Ray powder diffraction patterns of the products obtained by two different approaches were recorded using Bruker D8 Advance diffractometer (Cu-K α irradiation) at room temperature. The qualitative phase analysis was performed using the ICDD

PDF-2 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 was carried out by the Rietveld method using the DIFFRAC^{plus} TOPAS4.2 software (Bruker, Germany) and ICSD data (1997). The high temperature in situ XRD analysis was performed using the same diffractometer equipped with the high-temperature HTK-1200N (Anton Paar, Austria) chamber. The samples were heated step-by-step with the heating rate of 5 °C/min and were kept at the given temperature for 5 min before recording of XRD pattern.

The Raman spectra of initial and heat-treated at 200, 400, 600, 800 and 1000 °C ZrO₂–GeO₂ and HfO₂–GeO₂ xerogels were recorded at room temperature using the RFS/100 spectrometer (Bruker, Germany) equipped with the Nd:YAG laser (1064 nm wavelength, 100 mW power). The exposition time at given temperature was 1 h. At least 100 scans were recorded for each sample.

TG-DTA analysis was performed using NETZSCH STA 449F1 differential scanning calorimeter coupled with NETZSCH QMS 403D mass-spectrometer. The ZrO₂–GeO₂ and HfO₂–GeO₂ xerogels were heated with velocity of 5 °C/min in Ar at 1 bar.

3. Results and discussion

3.1. Heat-treatment of powdered Zr(Hf)O₂–GeO₂ mixtures (ceramic route)

3.1.1. XRD data

X-ray powder patterns of the heat-treated at 1300 °C ZrO₂–GeO₂ and HfO₂–GeO₂ mixtures are presented in Fig. 1a and b, respectively. According to XRD data, ZrGeO₄ phase is the main phase for the ZrO₂–GeO₂=1:1 mixture (Fig. 1a). Quantitative analysis of XRD pattern gives rise 98% (wt.) ZrGeO₄ yield. The rest appears to be related to Zr₃GeO₈ phase. Indeed, the strongest peak of this phase is detected in the XRD pattern as shoulder at $2\theta=30.5^\circ$. No initial oxides were detected by the XRD analysis. It must not be excluded that a deficiency in GeO₂ that arises as a result of slow evaporation of GeO₂ at the synthesis temperature (1300 °C) leads to the formation of two-phase product. Experimental powder pattern of ZrGeO₄ has two mismatches with ICDD PDF pattern (position and hkl indexes of most intensive reflex and intensity of 204 reflex); however, it is in good agreement with powder pattern calculated using ICSD record #29-262 (Fig. 2). Probably, the entry of ICDD PDF database for ZrGeO₄ should be refined.

As one can see from Fig. 1a, the heating of ZrO₂:GeO₂=3:1 mixture results in the formation of Zr₃GeO₈ as main phase. Together with Zr₃GeO₈, a minor quantity of ZrGeO₄ is observed too (as a shoulder at $2\theta=31.2^\circ$). The content of the main product is 94% (wt.).

Reaction of HfO₂ with GeO₂ in 1:1 ratio gives rise HfGeO₄ phase together m -HfO₂ as an impurity (Fig. 1b). For the heat-treated HfO₂:GeO₂=3:1 mixture no formation of Hf₃GeO₈ phase was detected by the XRD within the method limitation. Only small intensity shoulder at $2\theta=30.5^\circ$ is noticeable that could be related to the most intensive peak of Hf₃GeO₈ phase (PDF #16-800). An increase of time exposition at 1300 °C till 40 h with intermediate homogenization of mixture does not result in an appearance of noticeable quantity of Hf₃GeO₈ phase that was confirmed by X-ray studies, but the content of main phase HfGeO₄ in product slightly increases (96%).

The results of quantitative XRD analysis are presented in Fig. 3. Due to the difference in Zr(Hf) and Ge cation radii, the most appropriate value to identify the changes with increasing of GeO₂ content is the unit cell volume. According to data of qualitative

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