

# Synthesis of hafnium germanate ( $\text{HfGeO}_4$ ) by co-precipitation routes

J. Balencie <sup>a,\*</sup>, L. Levy <sup>b</sup>, J.-F. Hocheplé <sup>a</sup>

<sup>a</sup> *Laboratoire des Systèmes Colloïdaux dans les Procédés Industriels, CEP, Ecole des Mines de Paris, 60 Bld St-Michel 75006 Paris, France*

<sup>b</sup> *Nanobiotix, 32 rue du sentier, 75002 Paris, France*

Available online 3 January 2007

## Abstract

Hafnium germanate ( $\text{HfGeO}_4$ ) presents under X-ray excitation a high UV fluorescence at around 365 nm that may be used for X-ray imaging. Its synthesis by different co-precipitation routes with sodium hydroxide, ammonia, potassium hydroxide, dimethylamin and tetramethylammonium hydroxide was studied. Precipitated amorphous hydroxides were then washed, dried and calcined at 1100°C for 6 h to make  $\text{HfGeO}_4$  crystallize. Hydroxides and oxides were characterized by Fourier transformed infrared spectroscopy, X-ray diffraction and X-ray fluorescence. Hence we could emphasize importance and role of ammonium ions on the structure and optical properties of the synthesized products. More particularly, it has been demonstrated that only amorphous products precipitated in the presence of ammonium ions lead to single-phase  $\text{HfGeO}_4$ .

© 2006 Elsevier B.V. All rights reserved.

*Keywords:* Hafnium germanate; Co-precipitation; X-ray phosphor

## 1. Introduction

Hafnium germanate,  $\text{HfGeO}_4$ , has not been the object of many studies in literature (firstly studied by Lefèvre and Collongues [1,2] in the late fifties). However, it presents high UV fluorescence properties at around 365 nm under X-ray excitation. This is due to its high density ( $\approx 8.5 \text{ g/cm}^3$ ) and the presence of hafnium in the lattice, which provide an exceptional X-ray absorption. These properties are very suitable for X-ray imaging applications. Recently, new X-ray phosphors, including  $\text{HfGeO}_4$  [3–8], have been developed for medical intensifying screens. Traditional solid-state and precipitation methods have been used for the preparation of this germanate. This paper presents a parametric study of the synthesis of  $\text{HfGeO}_4$  by coprecipitation. The main advantage of this route consists in the close mixing of elements in amorphous products (before further processing), which is expected to have an impact on the crystallization of  $\text{HfGeO}_4$ : higher homogeneity of material, lower processing temperature and little grain size.

## 2. Experimental

### 2.1. Materials

$\text{HfOCl}_2 \cdot 8\text{H}_2\text{O}$  (Alfa Aesar, 98+%, 1.5% Zr) and  $\text{GeO}_2$  (Sigma-Aldrich, amorphous, glycol soluble, 99.99+%) were used as hafnium germanate precursors.  $\text{NH}_4\text{OH}$  (Alfa Aesar, ACS, 28–30%  $\text{NH}_3$ ), TMAH (Sigma-Aldrich, 25 wt.% solution in water), DMA (Fluka, purum, 40% in water, 7.9 M), NaOH (Prolabo, 97.6%) or KOH (Prolabo,  $\geq 85\%$ ) was used as precipitating agent.

### 2.2. Synthesis

Stoichiometric quantities of  $\text{HfOCl}_2 \cdot 8\text{H}_2\text{O}$  and amorphous  $\text{GeO}_2$  ( $1.9 \times 10^{-2} \text{ mol}$ ) were dissolved under stirring in respectively 100 and 150 mL de-ionized water. Both solutions were then mixed and continuously stirred. This was followed by a drop-by-drop addition of basic solution with the adequate stoichiometry. Precipitation occurred immediately and base addition went on until pH was 10–12 depending on the considered base. The final solution was kept under stirring for 30 min. The collected gel was then washed with de-ionized water. After that, it was lyophilized and then calcined at 1100 °C for 6 h.

\* Corresponding author. Tel.: +33 1 40 51 90 23; fax: +33 1 40 51 94 25.  
E-mail address: [jeremy.balencie@ensmp.fr](mailto:jeremy.balencie@ensmp.fr) (J. Balencie).

For the synthesis of the germanium precipitate, amorphous  $\text{GeO}_2$  was dissolved in distilled water. Then, some sodium chloride was added to increase the electrostatic repulsion and allow further precipitation. Precipitation occurred when ammonia was drop-by-drop added. Germanate gel was then washed by filtration and lyophilized.

Hafnium hydroxide was prepared by drop-by-drop addition of an ammonia solution into a hafnium dichloride ( $\text{HfOCl}_2$ ) solution. Amorphous precipitate was collected and washed by filtration before being lyophilized.

### 2.3. Characterization

Powder X-ray diffraction (XRD) experiments were made on a Bruker D8 diffractometer in  $\theta$ – $\theta$  configuration, using cobalt  $K\alpha_1$  radiation ( $\lambda=1.789 \text{ \AA}$ ) and equipped with a position sensitive detector. Crystallite size was evaluated from the width of isolated lines by applying Scherrer's formula:  $L_{\text{hkl}}=K\lambda / \Delta_{\text{hkl}} \cos \theta$ , where  $L_{\text{hkl}}$  is the length of the crystallite along the (hkl) direction,  $\Delta$  is the full-width at half-maximum of a given [hkl] peak corrected for instrumental broadening and  $K\alpha_1$  contribution,  $\lambda=1.789 \text{ \AA}$  and the structure factor was chosen as  $K=0.9$ .

Infrared spectra of the samples were recorded on a JASCO FT/IR-460Plus spectrometer. Dried powders were dispersed in KBr and then compressed under 10 tons into pellets. Blanks were realized with pure KBr pellets.

Powder X-ray fluorescence spectra of the samples were recorded on a Varian Cary Eclipse fluorescence spectrophotometer under emission mode. X-ray source was the same as for XRD and its energy was set up at 7 keV. X-ray fluorescence was measured and evaluated with optic fiber (silica/silica 0.22 NA, 200  $\mu\text{m}$ ) and fiber optic coupler with a fluorescence remote read probe used with a probe tip for solid sample.

## 3. Results and discussions

Hafnium germanate can be synthesized from a direct combination of the corresponding oxide precursors by using standard solid-state techniques. However this route presents some limitations due to (1) the high-temperature volatility of  $\text{GeO}_2$ , (2) the scheelite phase decomposition above 1300  $^\circ\text{C}$  and (3) the refractory nature of  $\text{HfO}_2$ . Besides all, main drawback of such a method is particle size limitation. It does not lead to nanoparticles but only to microparticles, which can be detrimental for the targeted application. Thus coprecipitation of hafnium and germanium precursors by different bases, i.e. sodium hydroxide (NaOH), ammonia ( $\text{NH}_3$ ), tetramethylammonium hydroxide (TMAH), potassium hydroxide (KOH) and dimethylamin (DMA) was fully investigated. In each case, except for TMAH, a stable precipitate is formed and then washed by filtration. In the case where the used base is TMAH, the formation of a very unstable precipitate that redissolved either during stirring or during washing is observed. This is surely due to the size of tetramethylammonium cation,  $\text{N}(\text{CH}_3)_4^+$ . In fact, Lambert [9] claimed that the mixed hydroxide is composed of hafnia and a germanate gel whose composition was not clearly defined. Nevertheless, some stable germanate

gels like  $(\text{NH}_4)_2\text{Ge}_5\text{O}_{11}\cdot 7\text{H}_2\text{O}$  [10,11] or  $(\text{NH}_4)_3\text{HfGe}_7\text{O}_{16}\cdot n\text{H}_2\text{O}$  [12,13] are well known. More generally, there exists a lot of germanates whose formula can be  $M_2\text{Ge}_2\text{O}_3$ ,  $M_2\text{Ge}_2\text{O}_5$ ,  $M_2\text{Ge}_4\text{O}_9$ ,  $M_2\text{Ge}_5\text{O}_{11}$  or  $M_3\text{HfGe}_7\text{O}_{16}\cdot n\text{H}_2\text{O}$  [14] where  $M$  is a monovalent cation. Some of them are only stable in solution but it clearly appears that the bigger the cation is the less stable are the corresponding germanates. Thus, tetramethylammonium cation is surely too big and heavy to form stable germanates. Ammonium germanate seems to be the most stable germanate and the easiest one to make whereas sodium or potash germanates are very often stable only in solution or need to be synthesized under hydrothermal conditions. This is a first evidence of the importance of ammonium cation on the synthesis of  $\text{HfGeO}_4$ .

### 3.1. IR spectroscopy

The different oxides were characterized with IR spectroscopy after calcination as shown on Fig. 1. There is no real difference between the different samples above 1000  $\text{cm}^{-1}$ . One can notice that each oxide is partially hydrated as one has an absorption band between 3340 and 3580  $\text{cm}^{-1}$  that corresponds to the stretching vibration of  $-\text{OH}$ . Furthermore it is confirmed by the peak at 1635  $\text{cm}^{-1}$  that corresponds to another vibration mode of  $-\text{OH}$ . Concerning the peak that appears at 1385  $\text{cm}^{-1}$ , it is an artefact due to KBr. However below 1000  $\text{cm}^{-1}$  there are some significant differences between samples. Those made with DMA (a) and NaOH (b) are very similar. Both spectra exhibit a little absorption band centred at 703  $\text{cm}^{-1}$ , which can be attributed to  $\text{Ge}-\text{O}_n$  vibrations. They also exhibit some bands centred at 550–560  $\text{cm}^{-1}$  and 417–430  $\text{cm}^{-1}$ . The first one may be attributed to  $\text{Ge}-\text{O}_n$  vibrations whereas the second one corresponds to  $\text{Hf}-\text{O}_n$  vibrations. This means that for hydroxides made by coprecipitation of Hf and Ge precursors with DMA or NaOH and then calcined, Ge and Hf have the same environment in both oxides. For the sample made with KOH (c), this environment is obviously different, at least for Ge, as we have some absorption bands at 788, 633, 530–535 and 417  $\text{cm}^{-1}$ . If the last peak corresponding to  $\text{Hf}-\text{O}_n$  vibration is the same as for the previous samples, the  $\text{Ge}-\text{O}_n$  vibrations are

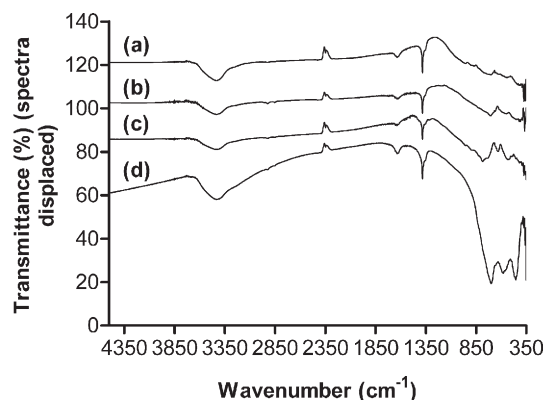


Fig. 1. FT-IR spectra of  $\text{HfGeO}_4$  made by coprecipitation with (a) DMA, (b) NaOH, (c) KOH and (d)  $\text{NH}_3$ .

Download English Version:

<https://daneshyari.com/en/article/1675496>

Download Persian Version:

<https://daneshyari.com/article/1675496>

[Daneshyari.com](https://daneshyari.com)