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Molten salt synthesis and characterization of non-doped hafnia

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The reactivity of hafnium tetrachloride towards the molten $NaNO_3$–KNO_3 medium is analyzed by thermogravimetry and XRD. After an investigation of the influence of various reaction parameters, an optimized synthesis procedure of the monoclinic variety of hafnia is proposed. The obtained powders are characterized.

Introduction

Hafnium dioxide (hafnia, HfO_2) exhibits structural and chemical properties similar to those of zirconia, however, it is a better refractory, its physical transformations being shifted towards high temperatures. Thus, the monoclinic (M) to tetragonal (T) transformation occurs reversibly in the temperature range 1750–1850 °C (1100–1200 °C for ZrO_2), with a volume change of less than half. The hafnia ceramics have not been frequently studied unlike their homologue ZrO_2, yet, they are considered to be potentially useful for structural applications. Consequently, hafnium tetrachloride could become more useful by transformation into hafnia.

Various methods were used for the preparation of hafnia: solid state reactions,[1] pyrolysis or flash decomposition of oxalate precursors,[2,3] the sol–gel method from alkoxides,[4] and the hydrothermal treatment of metallic hafnium dispersions.[5]

The present paper concerns the preparation of non-doped hafnia by reaction of $HfCl_4$ in a molten environment which generates O^{2-} ions by oxide reduction reactions. This method was previously applied successfully to the preparation of various oxide powders including pure zirconia,[6–9] yttria stabilized tetragonal zirconia,[10] TiO_2,[11] CeO_2[12] and Al_2O_3.[13]

Experimental

Starting materials

The hafnium precursor $HfCl_4$ was from Cézus-Chimie. The precursors of the oxide anions O^{2-} were alkali-metal nitrates (rectapur from Prolabo), $NaNO_3$ (mp 307 °C) and KNO_3 (mp 334 °C) used either alone or in an equimolar mixture (mp 225 °C).

Procedure and characterization

Hafnia powders were prepared by a previously described procedure[7,14] and characterized using the following techniques: chemical elemental analysis (CNRS microanalysis center, Vernaison, France), DTA (rate 10 °C min^{-1}, Setaram MDT A 85), XRD (Cu-Kα $\lambda = 1.5406$ Å, diffractometer for powders Siemens D500), granulometry by sedimentation (Horiba Capa 500 instrument, powders were dispersed *via* the procedure established by Samdi *et al.*[15]), BET (nitrogen adsorption, sorptometer Fisons 1900) and TEM (microscope Philips EM 300).

Some reactions were performed in the crucible of a Setaram G70 thermobalance to investigate the weight loss produced by gas release. Furthermore, the evolved gases were either analyzed by chromatography (GPC Hewlett Packard 5700A), in order to evidence the presence of oxygen or bubbled through a NaOH solution so as to evidence the formation of Cl_2 by iodometric determination of the ClO^- ions.

Results

Reactivity investigation

The reactivity of $HfCl_4$ was revealed by a two-step brown-red NO_2 evolution: a preliminary weak release of gas below the melting point of the nitrates (about 125 °C) and then a second strong release beginning simultaneously with melting around 225 °C, both occurring with an endothermic effect.[14] No insoluble reaction product was formed during the first step; the release was attributed to the start of the decomposition of the nitrates and also involved water present in the starting $HfCl_4$ (amount estimated at about 10 wt%[14]). The insoluble oxide formed at the end of the second step was identified by XRD to be the monoclinic variety of hafnia. The mass loss observed at 700 °C is about 53% of the starting hafnium tetrachloride mass (Fig. 1).

According to Kerridge,[16] the reduction of NO_3^- ions to NO_2 is balanced by the oxidation of oxide anions O^{2-} to oxygen. Therefore, the formation of hafnia should occur *via* reaction (1). However, the calculated mass loss, 67.4%, is significantly higher than that observed. Moreover, the presence of oxygen in the gaseous release was not detected by chromatography.

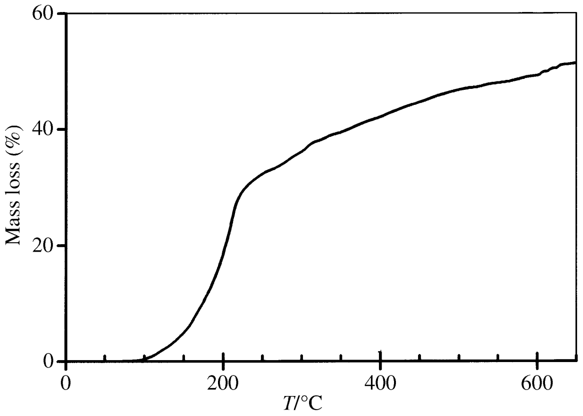

Fig. 1 Thermogravimetric analysis of the reaction of $HfCl_4$ + 7($NaNO_3$–KNO_3) (heating rate 2.5 °C min^{-1}).

$$\mathrm{HfCl_4 + 2NaNO_3 + 2KNO_3 \rightarrow HfO_2 + 4NO_2 + O_2 + 2NaCl + 2KCl} \qquad (1)$$

Miles[17] and Desimoni[18] have observed the oxidation of chloride ions in $LiNO_3$–KNO_3 and $NaNO_3$–KNO_3 media. Consequently, the formation of hafnia was also likely to occur *via* reaction (2) giving a calculated mass loss (50.8%) approaching the experimental one. Furthermore, the presence of hypochloride ions is evidenced in an alkaline solution after bubbling of the evolved gases.

$$\mathrm{HfCl_4 + NaNO_3 + KNO_3 \rightarrow HfO_2 + 2NO_2 + Cl_2 + NaCl + KCl} \qquad (2)$$

With the employed procedure the formation of hafnia is more likely to occur according to reaction (2) than to reaction (1). That the concentration of transition metal is significantly higher in our experiments that in Kerridge's might explain the discrepancy.

Influence of various reaction parameters on the characteristics of hafnia powders obtained

The influence of the reaction temperature, the time for which the temperature was maintained level, the nature of the alkali-metal nitrate medium, the excess of nitrates towards the stoichiometry of the reaction and the washing were investigated in order to optimize the synthesis procedure.

For reactions carried out for five hours (heating + level) the increase of the temperature from 250 to 500 °C involved a progressive evolution from an amorphous solid (250, 300 °C) to a crystallized monoclinic hafnia (500 °C) (Fig. 2). On annealing, the exothermic crystallization of the amorphous phase into monoclinic hafnia occurred (Fig. 3 and 4); the temperature and amplitude of the DTA peak decreased simultaneously with the proportion of the amorphous phase. The chemical analysis revealed very low amounts of alkali metals, nitrate and chloride ions, except for the sample prepared at 250 °C (Table 1). The increase in the amount of hafnium and the decrease of the fire loss (weight loss produced by annealing or calcination) were related to an efficiency of the oven-drying, 110 °C lower for the amorphous phase than for the crystallized hafnia. The mean size of the crystallites (XRD line broadening) and the width of the granulometric distribution were regularly increased by the elevation of the temperature, respectively from 3 to 8 nm and 4 to 11 µm.[14]

For reactions performed at 350 °C, the lengthening of the time for which the temperature was maintained level from 1 to 48 hours induced only a weak amelioration of the crystallinity (Fig. 5). The sample prepared for 48 hours had similar characteristics to that of a sample obtained with a level of 1.5 hours at 400 °C.

For reactions carried out with a level at 450 °C for 1 hour, the decrease of the crystallite mean size, following the sequence KNO_3, $NaNO_3$, $NaNO_3$–KNO_3 (Fig. 6), was related to the difference between the reaction temperature and the melting temperature of the nitrate medium; the increase of ΔT favoured the supersaturation in hafnium and consequently the nucleation step of HfO_2 at the cost of crystal growth. Indeed, it was assumed that the reaction proceeded *via* a dissolution–precipitation mechanism involving a Lux–Flood acid–base reaction, as was previously concluded for the formation of ZrO_2[6] or TiO_2.[11] Besides the peaks of monoclinic HfO_2, the XRD pattern of the powder prepared in $NaNO_3$ exhibited the strongest peak of tetragonal HfO_2, the formation of which was linked to an amount of sodium in the powder (0.52 wt%) about ten times higher than in the sample prepared in $NaNO_3$–KNO_3.

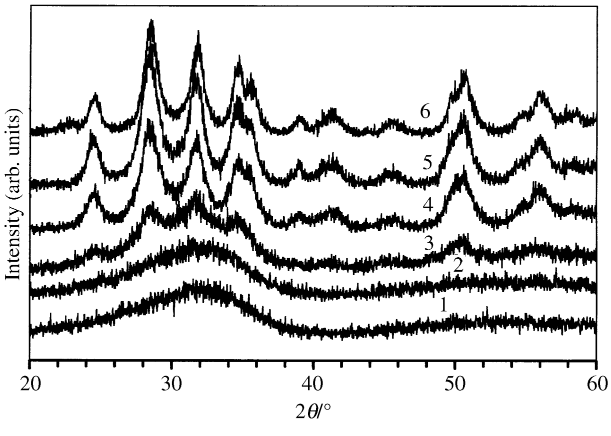

Fig. 2 Influence of the reaction temperature on the XRD pattern of hafnia samples obtained by reaction of $HfCl_4 + 7(NaNO_3$–$KNO_3)$ mixtures for five hours: (1) 250; (2) 300; (3) 350; (4) 400; (5) 450; (6) 500 °C.

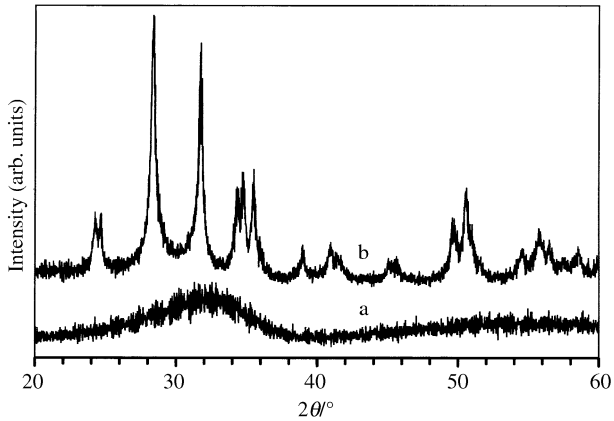

Fig. 3 Effect of annealing on the XRD pattern of the hafnia powder prepared from the reaction of $HfCl_4 + 7(NaNO_3$–$KNO_3)$ at 250 °C for five hours: heating stopped at 450 °C, *i.e.* below the DTA crystallization peak (a), at 600 °C, *i.e.* above the crystallization peak (b).

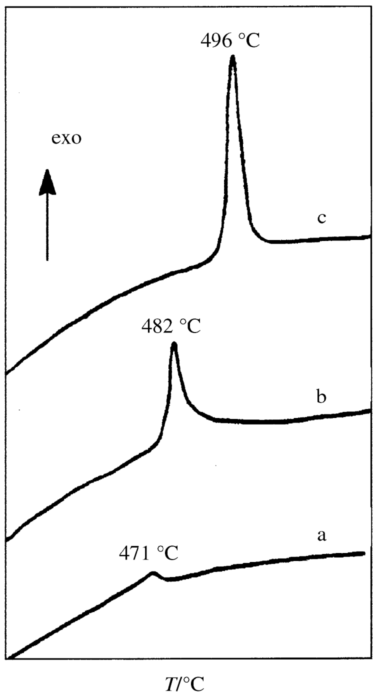

Fig. 4 DTA curve of hafnia samples prepared from reaction of $HfCl_4 + 7(NaNO_3$–$KNO_3)$ mixtures for five hours at 450 °C (a), 300 °C (b) and 250 °C (c).

Table 1 Chemical analysis (mass %) of the constitutive elements and fire loss (mass %) of the samples obtained from the reactions of $HfCl_4 + 7(NaNO_3–KNO_3)$ at various temperatures for five hours

	Element					
Reaction temperature/°C	N	Cl	K	Na	Hf	Fire loss
250	0.180	0.26	$\leqslant$0.05	0.05	72.9	14.1
300	<0.04	<0.05	$\leqslant$0.05	0.02	72.8	14.0
400	<0.04	<0.05	$\leqslant$0.05	0.03	75.3	10.9
500	<0.04	<0.05	$\leqslant$0.05	0.05	81.3	4.0

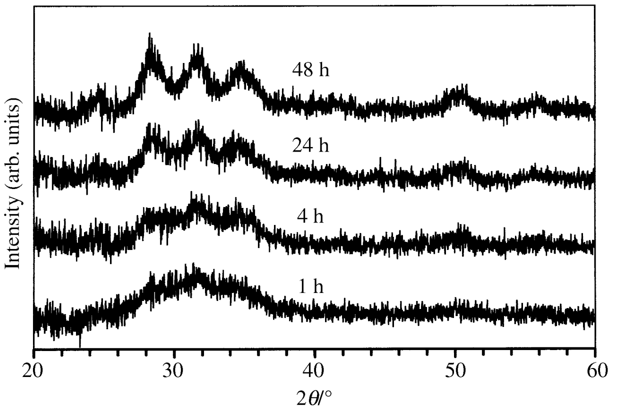

Fig. 5 Influence of the reaction time on the XRD pattern of hafnia samples prepared from reaction of $HfCl_4 + 7(NaNO_3–KNO_3)$ at 350 °C.

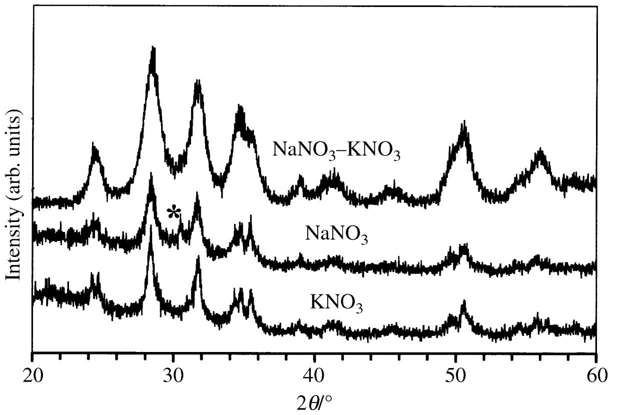

Fig. 6 Influence of the nature of the alkali-metal nitrates on the XRD pattern of the hafnia samples prepared from reaction of $HfCl_4 + 14\ XNO_3$ at 450 °C for 1 hour (X = Na, K or 0.5 Na + 0.5 K). *Indicates tetragonal HfO_2.

It was shown that reactions performed with a level at 450 °C for 1 hour were complete when the molar ratio of $NaNO_3–KNO_3$ to $HfCl_4$ reached seven times the stoichiometric ratio with regard to eqn. (2).[14] Furthermore, it was observed that a last washing with isopropanol strongly decreased the size of the agglomerates of the hafnia powders. A similar effect was previously evidenced for zirconia powders[19,20] and explained as being due to the replacement of the surface OH groups by ethoxy groups which prevent the formation of hydrogen bonds which can be transformed into oxygen bridges on calcination.

Finally, the monoclinic hafnia powders were prepared according to the following optimized procedure. Mixtures of $HfCl_4$ and $NaNO_3–KNO_3$ in the molar ratio 1 Hf to 14 NO_3^- were heated at 450 °C (rate 150 °C h^{-1}) and held for 1 hour. The reaction medium was quenched at room temperature, then the soluble salts were extracted with water and the hafnia powder washed with isopropanol and oven dried at 110 °C for 24 hours. The powders obtained were constituted of nanosized crystallites gathered in soft agglomerates (Fig. 7) with sizes regularly spread from a few tens of nm to 10 μm (maximum at 2 μm). The crystallite sizes measured on micrographs (5–6 nm) agreed with the mean size estimated from XRD peak broadening (7 nm). The specific surface area was about 110 $m^2\ g^{-1}$ and the porous volume 170 $mm^3\ g^{-1}$ with the size of the pores spread from a few nm to 2 μm (maximum at 0.6 μm). The lattice parameters refined with silicon as internal standard were in fair agreement with those given in the literature[21] (Table 2). The chemical analysis data were intermediate between those obtained for samples prepared at 400 and 500 °C (Table 1).

Discussion

The reactivity of $HfCl_4$ with the molten nitrate media, KNO_3 or equimolar $KNO_3–NaNO_3$, at 450 °C, leads to monoclinic HfO_2 whereas ZrO_2, obtained from the same media at the same temperature, crystallizes in its tetragonal variety alone or in the presence of a small proportion of the monoclinic variety. The formation of metastable T ZrO_2 was also observed for powders prepared by other methods (hydrothermal synthesis, precipitation). On the contrary, the crystallization of T HfO_2 is quite rare. Lakhlifi[22] prepared T HfO_2, containing a small proportion of the M phase, by thermogravimetry at controlled rate (ATVC) of hafnyl oxalic acid under vacuum up to 430 °C. The powder obtained was black due to the presence of superficial carbon which is eliminated by calcination under O_2 up to 900 °C. The calcined powder became white though the stabilization of the T variety could be a result of the presence of traces of carbon. Indeed, Samdi[23] justified the formation of metastable tetragonal zirconia in the pyrolysis of zirconium acetate by the presence of residual carbon in such white powders.

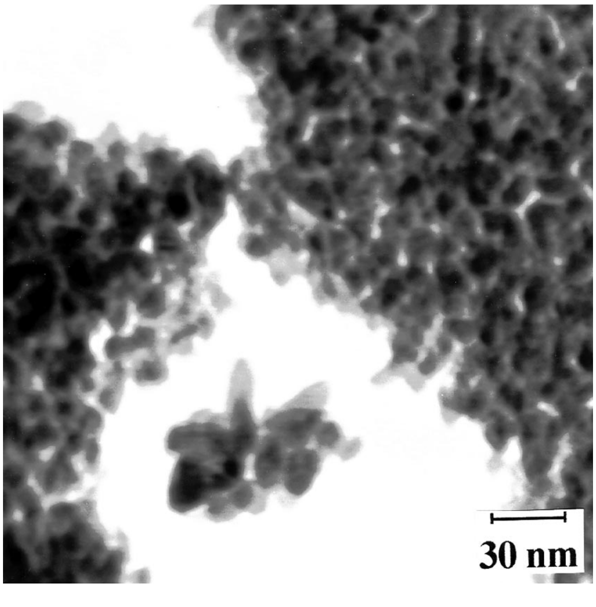

Fig. 7 TEM micrograph of a hafnia powder prepared following the optimized procedure.

Table 2 Comparison between the lattice parameters given in the literature[21] for monoclinic HfO_2 and the experimental data for a monoclinic hafnia sample obtained following the optimized procedure

Lattice parameters	Experimental data	ICDD no 43-1017
a/Å	5.099(2)	5.116
b/Å	5.198(2)	5.182
c/Å	5.292(2)	5.285
β/°	99/233(5)	99.259

The formation of T HfO_2 in small proportions beside the M variety is assumed in the reaction of $HfCl_4$ with molten $NaNO_3$ and attributed to the presence of sodium in the lattice. This was also observed by Hunter,[24] in the pyrolysis of hafnium oxychloride and hydroxide near 450 °C and, by hot isostatic pressing of Eu-doped HfO_2. In the first case the presence of T HfO_2 was attributed to a size effect with a critical diameter experimentally stated at 10 nm. In the latter case, the particles diameter was five times higher than their critical diameter, but the stabilization was ascribed to stresses induced by the hot pressing.

Numerous investigations on ZrO_2 enhanced the role of crystallite size and of stress on the polymorphic transformation M–T. Bailey[25] and Garvie[26] proposed an equation, taking into account for the two phases the density and the surface energy, allowing the calculation of a critical diameter of 33 nm above which the transformation T to M occurs. According to Hunter,[24] the same approach leads to a significantly lower critical diameter of 3.6 nm for HfO_2, a value so small that it would be impossible to retain crystallites of pure T HfO_2 at room temperature.

The hafnia powders, prepared from the reaction of $HfCl_4$ with molten KNO_3 or equimolar $NaNO_3$–KNO_3, crystallize in the M variety and consist of crystallites with sizes in the range 4 to 10 nm. These values are lower than the ones obtained experimentally by Hunter for the T crystallites in hafnia prepared by pyrolysis of $HfCl_4$ or $Hf(OH)_4$, but higher than the critical diameter calculated from thermodynamic data. For reasons which could be related to the presence of impurities at very low concentration, the critical diameter for the retention of T crystallites should be lower for hafnia prepared by precipitation from KNO_3 or $NaNO_3$–KNO_3 molten media than for hafnia prepared by pyrolysis, and should become very close to the calculated value. In molten $NaNO_3$ medium the presence of amounts of sodium in the powders, tenfold higher than in hafnia precipitated from KNO_3 or $NaNO_3$–KNO_3, raises the critical diameter to somewhere in the range 4 to 10 nm. Hence, the formation of mixtures of tetragonal and monoclinic crystallites in the powders constituted of crystallites with sizes in the range 4 to 10 nm would be justified.

Conclusion

The reactivity of $HfCl_4$ toward molten KNO_3 and $NaNO_3$–KNO_3 media leads, *via* a Lux–Flood acid–base reaction, to the precipitation of hafnia. Transformations carried out below 400 °C produce a mixture of monoclinic hafnia and an amorphous phase whose proportion is all the more significant as the reaction temperature is low. Transformations performed at 450 °C give only crystallized monoclinic hafnia.

An optimized procedure is proposed. It leads to monoclinic hafnia powders consisting of submicronic soft agglomerates exhibiting an intra-agglomerate porosity due to the stacking of nanosized crystallites. The powders are characterized by a large specific surface area and a purity acceptable for ceramic applications.

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