Crystal structure of a new $HfO(OH)_2$ oxyhydroxide

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The crystal structure of a new hafnium oxyhydroxide obtained by an ion-exchange reaction from a Li_2HfO_3 precursor has been solved by a direct method and refined using Rietveld full profile fitting based on X-ray powder diffraction data. $HfO(OH)_2$ crystallizes in a $P2_1/c$ monoclinic unit cell (a = 5.5578(5) Å, b = 9.0701(10) Å, c = 5.7174(5) Å, β = 119.746(5)°); its structure can be described as a framework formed by edge-sharing HfO_6 octahedra connected to each other via vertices. In addition, an analysis of the atomic pair distribution function obtained using synchrotron radiation was used to confirm the model and to describe fine-structure features.

Key words: hafnium oxyhydroxide, crystal structure, powder diffraction, pair distribution function

I. INTRODUCTION

Hafnium oxyhydroxide (metahafnium acid) has been for a long time considered to be an amorphous $HfO_2 \times H_2O$ compound, which can be obtained as a precipitate during the neutralization reaction between a soluble hafnium salt and an alkali (Knunyants, 1988; Nikolsky, 1971). However, in our recent studies it has been shown that the use of an ion exchange reaction with Li_2HfO_3 as a precursor allows to synthesize a crystalline $HfO(OH)_2$ compound as an individual phase (Baklanova *et al*., 2011). In the same way, other oxyhydroxides from the IVB group of the periodic table ($TiO(OH)_2$ and $ZrO(OH)_2$) have been synthesized and their physico-chemical properties have been studied recently (Baklanova *et al*., 2011; Orera *et al*., 2005; Denisova *et al.*, 2006; Yawata, 2006; Tarakina *et al*., 2010a; Tarakina *et al*., 2010b; Tarakina *et al*., 2011). However, only the crystal structure of $TiO(OH)_2$ has been described (Tarakina *et al*.,

 0885-7156/2013/28(S2)/S2/1/$18.00 ©2013 JCPDS-ICDD

https://doi.org/10.1017/S0885715613000791 Published online by Cambridge University Press

2010a; Tarakina *et al*., 2010b; Tarakina *et al*., 2011). It has been shown that titanium oxyhydroxide has a layered structure closely related to the structure of the low-temperature modification of the Li_2TiO_3 salt; elements of disorder characteristic of the structure of the precursor are preserved in the structure of the oxyhydroxide as well.

The main goal of this study is to solve and refine the crystal structure of the new $HfO(OH)_2$ compound using information about the structure of the related Li_2HfO_3 salt. Such knowledge will contribute to an understanding of its physical properties and will be of help in guiding the design of possible applications.

II. EXPERIMENT

$HfO(OH)_2$ powder was synthesized from Li_2HfO_3 precursor by an ion exchange reaction**.** The precursor was obtained by the sol-gel citrate route. For this, HfO_2 (99.9%) was dissolved in a water solution of hydrofluoric acid (40 mass%). The obtained solution was steamed for a long time in order to remove remaining fluoride ions and then 10 times diluted with distilled water. A NH_4OH solution (12.5 mass%) was added to the reaction mixture. The latter was kept at room temperature during 4-5 hours in order to reach complete precipitation of Hf ions in hydrated form. The obtained gel was separated from the solution by decantation, washed several times in distilled water, filtered and dried in air. Then, the freshly synthesized $HfO_2{\times}4.5H_2O$ powder was dissolved in diluted HNO_3 (2M) with continuous stirring and heating at 150 °C; a stoichiometric amount of Li_2CO_3 and an amount of citric acid $C_6H_8O_7{\cdot}2H_2O$ sufficient for complex formation were added to the reaction mixture. The obtained solution was then boiled down at ~250 °C under constant stirring till the formation of a dry residual solid. Calcining of the residual solid powder was performed in three steps at temperatures of 300 °C (2 hours), 650 °C (10 hours) and 700 °C (4 hours), with intermediate cooling and regrinding in an agate mortar at each stage. A part of the obtained Li_2HfO_3 powder was used for a structural study, the rest was used as a precursor for the $HfO(OH)_2$ synthesis.

Li_2HfO_3 was kept in an acetic acid aqueous solution (0.05 mol/l) at 60° C during 14 hours. The extent of exchange of Li^+ by H^+ was controlled using a pH-meter (Anion 4100) with a glass electrode. The ratio between "solid and liquid" phases was 1 g/l. The final product, $HfO(OH)_2$, was washed in distilled water and dried in air until constant mass was achieved.

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X-ray powder diffraction (XRD) patterns were collected at room temperature on a transmission STADI-P (STOE, Germany) diffractometer equipped with a linear mini-PSD detector using CuKα_1 radiation in the 2θ range 5° - 120° with a step of 0.02°. Polycrystalline silicon (a = 5.43075(5) Å) was used as an external standard. The phase purities of the samples were checked by comparing their XRD patterns with those in the Powder diffraction file - PDF2 database (ICDD, USA, release 2010). The GSAS program package (Toby, 2001; Larson and Von Dreele, 2004) was used for structure refinement from powder data.

Synchrotron radiation scattering experiments were carried out at beamline BW5 (DESY, Hamburg, Germany) at a primary energy of 100 keV, i.e. a wavelength of 0.123984 Å, using a Perkin-Elmer flat panel area detector at room temperature. The samples were loaded into a capillary with outer diameter equal to 1.8 mm. For background corrections a spectrum from an empty capillary with the same diameter was collected. Refinement of the pair distribution function (PDF) data was carried out with the PDFgui software (Farrow *et al*., 2007).

III. RESULTS AND DISCUSSION

The XRD pattern of Li_2HfO_3 has been indexed in a monoclinic unit cell with the following constants: a = 5.4149(2) Å, b = 8.9794(4) Å, c = 5.3991(2) Å, β = 112.831(3)°. An analysis of systematically absent reflections ($hk0$: $h+k = 2n$; $h0l$: $h = 2n$, $l = 2n$; $0k0$: $k = 2n$) in the XRD pattern indicates two possible space groups, Cc and $C2/c$. The structure of the monoclinic modification of Li_2ZrO_3 (sp.gr. $C2/c$) (Hodeau *et al*., 1982) was used as a starting model for the refinement. The peak profiles were fitted with a pseudo-Voigt function, $I(2\theta) = xL(2\theta) + (1 - x)G(2\theta)$ (where L and G are the Lorentzian and Gaussian parts, respectively). The angular dependence of the peak width was described by the relation $(\mathrm{FWHM})^2 = U \tan^2\theta + V \tan\theta + W$, where FWHM is the full linewidth at half maximum. The background level was described by a 36^{th}-order Chebyshev polynomial. The absorption correction function for a flat plate sample in transmission geometry has been applied. At the final steps of the refinement mixed occupancies of the metal sites were introduced. The total chemical composition of the compound obtained from the refinement is $Li_{2.04}Hf_{0.96}O_3$, which is slightly different from the nominal composition. Refined atomic coordinates and temperature factors can be found in Table I. The calculated, observed and difference XRD patterns are shown in Fig. 1. Li_2HfO_3 oxides can be described as a cubic close-packing of oxygen atoms in the octahedral voids between which metals are placed. The unit cell

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consists of two mixed metal layers with a honeycomb arrangement of Li atoms in it. These layers are stacked on top of each other along the *c* axis with a shift of 1/6 along the *b* direction. In spite of a considerable decrease of the *R*-values, the introduction of mixed occupancies of the metal positions does not lead to a perfect profile fit: the intensities of some reflections (021, -202, -131, 131, etc.) are not described correctly and a peculiar broadening of the peaks in the 2θ range 18-40° is observed. These facts indicate serious limitations of the present fit. A more complex approach has to be proposed in order to control the refinement process better. Probably the small and anisotropic size of coherent scattering domains has to be included, as well as possible structural defects, as demonstrated for the Li_2TiO_3 compound (Tarakina *et al*., 2010a; Tarakina *et al*., 2010b; Tarakina *et al*., 2011).

Table I. Atomic coordinates and isotropic thermal parameters for Li_2HfO_3.

Atom	*x/a*	*y/b*	*z/c*	Occupancy	U_{iso}×100, Å^2
Hf/Li1	0	0.08992(26)	0.25	0.804(9)/0.191(9)	3.18(13)
Li1/Hf	0	0.4167(15)	0.25	0.886(3)/0.114(3)	3.06(30)
Li2/Hf	0	0.7528(27)	0.25	0.963(2)/0.037(3)	2.00(60)
O1	0.25	0.25	0.5	1.0	2.5
O2	0.2790(13)	0.5711(9)	0.4913(14)	1.0	2.5

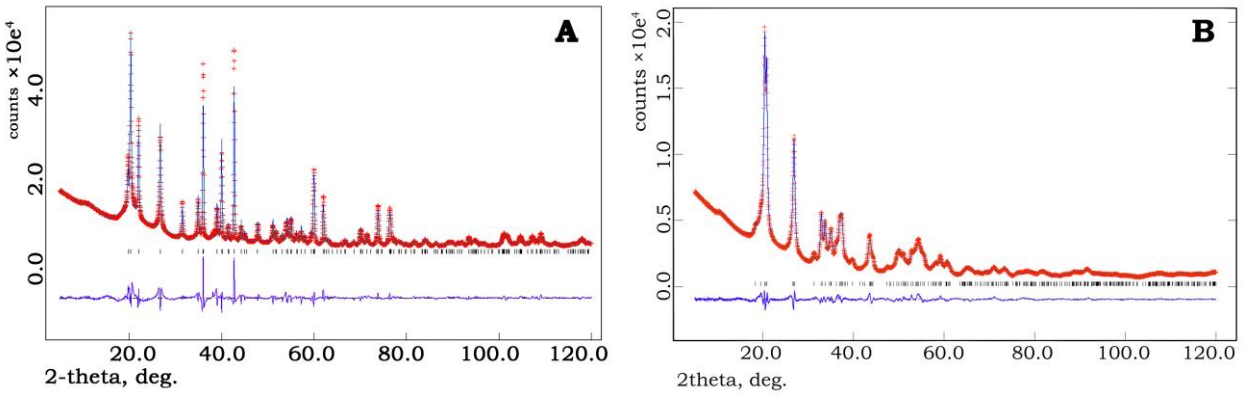


Figure 1. Observed (crosses), calculated (solid line) and difference (bottom line) X-ray powder diffraction patterns of (a) Li_2HfO_3 and (b) $HfO(OH)_2$. The corresponding reliability (*wRp*, R_p, $R(F^2)$) parameters are *wRp*=8.66%, *Rp*=6.17%, $R(F^2)$=8.25% and 3.64%, 2.65%, 2.45% for Li_2HfO_3 and $HfO(OH)_2$, respectively.

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Considering that $HfO(OH)_2$ has been obtained from a lithium salt precursor by ion exchange reactions and that the related positions of most of the peaks in the XRD patterns of the oxyhydroxide remain unchanged compared with those in the pattern of the salts, we propose that the crystal structure of $HfO(OH)_2$ is very close to the structure of Li_2HfO_3. The diffraction pattern has been indexed in a $P2_1/c$ monoclinic space group with unit cell constants a = 5.5578(5) Å, b = 9.0701(10) Å, c = 5.7174(5) Å, β = 119.746(5)°. The crystal structure has been solved using the EXPO2009 program suite (Altomare *et al*., 2009). The resulting structure model of $HfO(OH)_2$ (Fig. 2) was refined with GSAS (Toby, 2001; Larson and Von Dreele, 2004) using the X-ray powder diffraction data.

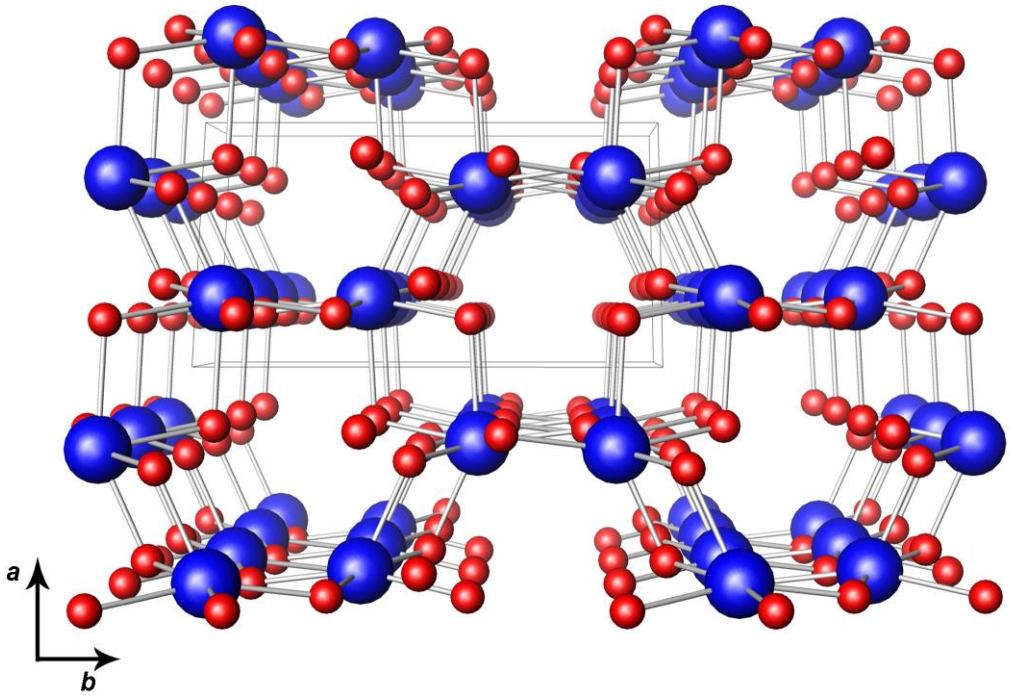


Figure 2. Perspective view on the *ab* plane of the $HfO(OH)_2$ structure. Hf atoms are blue spheres, oxygens are red spheres.

Our XRD data show significant broadening of Bragg reflections. This broadening can be due to several reasons: lamellar shape of the domains, small size of the domains, stacking faults, poor crystallinity, etc. In order to describe this broadening, a profile function employing a multi-term Simpson's rule integration of the pseudo-Voigt function has been used (Larson and Von Dreele, 2004; Howard, 1982; Thompson *et al*., 1987). Application of this function allows describing the profile when one set of reflections has a different domain size anisotropy than the other set. This

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effect can appear on the diffraction patterns of e.g. samples with stacking faults, broadening some reflections and leaving a sublattice of sharp reflections unmodified by the stacking fault. The refined atomic coordinates, temperature factors and selected interatomic distances are given in Tables II and III. The calculated, observed and difference XRD patterns are shown in Fig. 1.

Table II. Atomic coordinates and isotropic thermal parameters for $HfO(OH)_2$. Occupancies are equal to 1 for all atoms.

Atom	*x/a*	*y/b*	*z/c*	$U_{iso}\times100$, Å^2
Hf	0.7235(5)	0.10294(19)	-0.04625(35)	2.50
O1	0.805(4)	-0.0658(31)	-0.1954(31)	2.50
O2 (OH)	0.314(4)	0.0396(22)	-0.2279(30)	2.50
O3 (OH)	0.668(4)	0.1535(19)	-0.4753(40)	2.50

Table III. Selected interatomic distances (Å) for $HfO(OH)_2$. Average values are given in boldface, the relative degree of distortion of octahedra in italic.

	$HfO(OH)_2$	
Bond	X-ray	PDF
Hf–O(1)	1.912(25)	2.231(2)
Hf-O(1)	2.302(17)	2.264(7)
Hf-O(2)	2.062(19)	2.077(1)
Hf-O(2)	2.119(15)	2.126(3)
Hf-O(3)	2.362(17)	2.294(6)
Hf-O(3)	2.294(17)	2.112(4)
	2.175	**2.185**
	0.18	*0.09*

Unfortunately, $HfO(OH)_2$ is not stable under a high voltage electron beam, therefore its local structure cannot be studied directly using transmission electron microscopy techniques. To get

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more details on the local structure of the oxyhydroxide we tried the same structural models to fit the experimental PDF (Fig. 3).

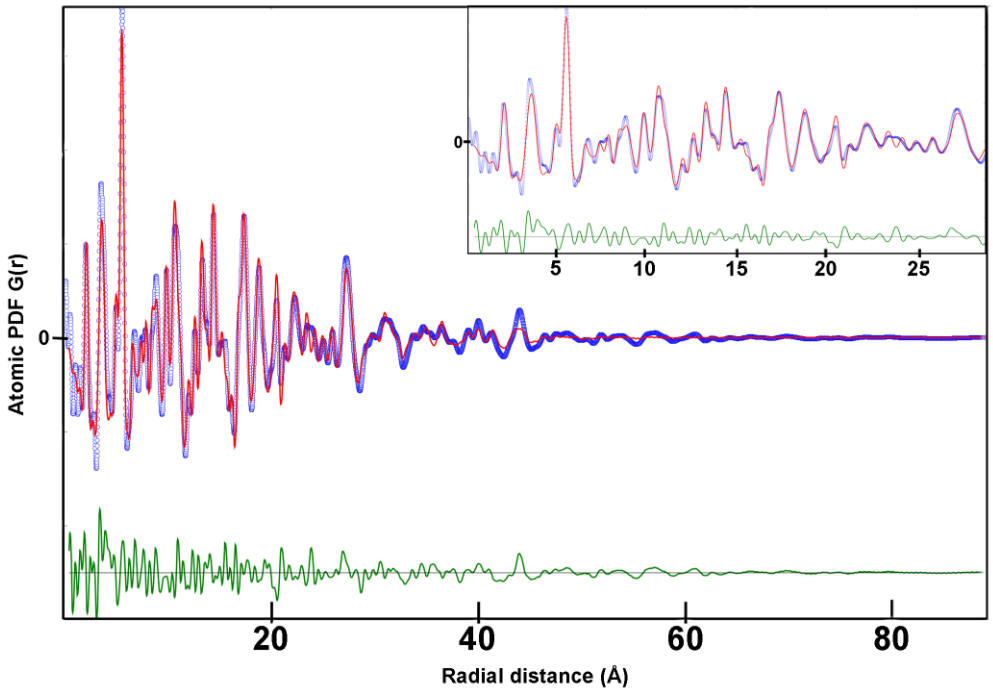


Figure 3. Experimental (circles) and model (lines) atomic PDFs $G(r)$ for $HfO(OH)_2$. The residual difference between the experimental data and the model data is given in the lower part of the plots. The goodness-of-fit is R_w = 26.3%.

The PDF technique uses a least-squares procedure to compare experimental and model (PDF) data calculated from a proposed structural model, similar to the Rietveld refinement. The structural parameters of the model (unit cell constants, atomic coordinates and thermal factors) have been included into the refinement, as well as instrumental parameters and the average size of coherently scattering domains (as spherical particles). The model PDFs were convoluted with a Sinc function (Billinge, 1998) before comparing with experimental results in order to take into account the finite Q_{max} of the diffraction data. The model obtained from the X-ray powder diffraction data gives a very good description of the PDF data in the range r = 0-30 Å. In order to describe the spectrum at higher values of r, a coherent domain size has been introduced into the refinement, resulting in convergence at the value ~ 70 Å. It is worth to mention that the distortion of Hf octahedra was found to be 0.09 from the PDF data, and 0.18 from the Rietveld refinement (Table III). This can be the evidence of size and shape dependence, which is described more correctly by the PDF analysis. The presence of the anisotropic domain size is the main reason for the fast decay of the PDF function and the broad and asymmetric shape of the

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peaks in the X-ray powder diffraction pattern. Summarizing, we can say that $HfO(OH)_2$ keeps the basic motif of the related Li_2HfO_3 salt, in such a way that during the ion exchange reaction the pairs of Hf octahedra are preserved in the structure. However, their rotation in the *ab* plane destroys the oxygen close-packed arrangement and leads to a lowering of the symmetry, so that the structure can be described as a framework formed by pairs of edge-sharing HfO_6 octahedra connected to each other via vertices. The presence of disorder in the precursor is most probably retained in the structure of the oxyhydroxide. An additional neutron experiment is essential to get a correct description of the disorder and to define the positions of the hydrogen atoms.

IV CONCLUSIONS

The crystal structure of a new hafnium oxyhydroxide obtained by an ion-exchange reaction from a Li_2HfO_3 precursor has been solved and refined. It crystallizes in the $P2_1/c$ monoclinic unit cell (a = 5.5578(5) Å, b = 9.0701(10) Å, c = 5.7174(5) Å, β = 119.746(5)°) and its structure can be described as a framework formed by pairs of edge-sharing HfO_6 octahedra connected to each other via vertices. The fast decay of the PDF function and the broad and asymmetric shape of the peaks in the X-ray powder diffraction pattern of the oxyhydroxide can be mainly attributed to the anisotropic size of domains.

Acknowledgement. N.V.T. acknowledges funding by the Bavarian Ministry of Sciences, Research and the Arts. The authors acknowledge the access to the user facility for X–ray structure analysis at the Institute of Solid State Chemistry, UB RAS (Ekaterinburg, Russia).

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