

The high crystal quality of the as-grown crystals as well as the efficiency of the substitution was pointed out by room-temperature single-crystal X-Ray Diffraction (XRD) data. The evolution of the structural distortion with the rise of substitution rate from ambient temperature to high temperature (near 1050°C) was followed by powder X-Ray Diffraction and Raman scattering analyses. Both electrical and optical twins were refined using Shelxl 97 software. The substitution rate and its distribution homogeneity along different crystal were carefully examined by Energy Dispersive X-ray analyses.

Keywords: quartz, solid-solution, X-ray

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Crystallographic and kinetic study of octa-coordinated hafnium(IV) complexes

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Zirconium and hafnium show extremely similar chemical properties and occur together in nature. Zirconium ore (*a.k.a.* Zircon – ZrSiO₄) is found to always contain hafnium as an impurity (1-5%), and separation of these two metals is very difficult due to their near identical chemical properties.

The aim of this study was to investigate the chelating behaviour of tetrachlorido hafnium(IV) (HfCl₄) with different organic bidentate ligands e.g. trifluoroacetylacetone (tfaaH), hexa-fluoroacetylacetone (hfaaH) and 8-hydroxyquinoline derivatives (OxH) and the characterization of the new compounds obtained from this by means of single crystal X-ray crystallography and UV/Vis spectroscopy. Optimal reaction conditions was found for different substituted L,L'-bidentate halido-hafnium complexes. Any small differences in solution behaviour, whether it being reaction mechanism, solubility, coordination modes, equilibrium behaviour, etc., could possibly be exploited in developing novel separation techniques for the two metals. The structures of six new complexes, namely the [Hf(tfaa)₄] [1], [Hf(OH)(hfaa)₃] [2], Hf(dbm)₄ [3], [Hf(Ox)₄] [4] [5], [Hf(5,7-diMe(Ox))₄], [Hf(5,7-diBr(Ox))₄], [Hf(5,7-diCl(Ox))₄] were determined. This enabled the identification of products for kinetic studies and increased the available pool of these rare compounds in literature. The crystallographic characterization of all these complexes will be presented.

As part of the preliminary kinetic investigation the formation of the above complexes, i.e., the stepwise reactions between HfCl₄ and OxH ligands were followed by means of stopped-flow and UV/Vis spectroscopy. A total of five reactions were observed for the stepwise coordination of OxH to the HfCl₄ complex.

[1] J.A. Viljoen, A. Roodt, Muller, *Acta Cryst.* **2008**, E64, m838-m840. [2] A.J. Viljoen, A. Roodt, H.G. Visser, M. Steyn *Acta Cryst.* **2009**, E66, m1367-m1368. [3] J.A. Viljoen, A. Roodt, H.G. Visser, *Acta Cryst.* **2010**, E66, m1053-m1054. [4] J.A. Viljoen, A. Roodt, H.G. Visser, M. Steyn *Acta Cryst.* **2009**, E66, m1514-m1515. [5] J.A. Viljoen, A. Roodt, H.G. Visser, *Acta Cryst.* **2010**, E66, m603-m604.

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Anion order in perovskite RTa(O,N)₃ and pyrochlore

R₂Ta₂(O,N)₇ where R = La, Ce, Pr

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Anion order in RTaON₂ perovskites and R₂Ta₂O₅N₂ pyrochlores is closely tied to physical properties, particularly the dielectric properties. Reports on alkaline-earth ATaO₂N perovskites vary from fully ordered to completely disordered. [1], [2], [3], [4], [5], [6]. Recent studies of SrTaO₂N using variable temperature NPD provide the most compelling evidence to date of local cis-ordered TaO₄N₂ units connecting to make zig-zag chains.[7] Does this phenomena persist when the oxide anions are in minority (local TaO₂N₄ units) such as the case with perovskite CeTaON₂ and PrTaON₂?

The symmetry of ATaO₂N and RTaON₂ oxynitride perovskites can be lowered from the cubic aristotype by {a} octahedral tilting, {b} anion ordering, and/or {c} out-of-center displacements of Ta(V) ions. Various combinations of these distortions lead to a large number of possible structures. Differentiating these structures using X-ray diffraction can be challenging as the distortions are subtle and the anion order is not necessarily complete. In this presentation we use symmetry analysis, computational modeling (total energy minimization), and Raman spectroscopy to augment diffraction studies of structural distortions in these compounds.

Oxynitrides that crystallize with structures that possess chemically distinct anion sites often show considerable chemical order of the oxide and nitride ions. One structure type that offers this possibility is the pyrochlore structure. Oxynitride pyrochlores R₂Ta₂O₅N₂ where R = La, Pr, Ce have been prepared for the first time using a unique, selective-oxidation precursor, BaO₂. Synthesis and characterization of these compounds will be presented, including a discussion of site ordering preferences of the anions.

[1] E. Gunther, et. al. *Zeitschrift fuer Anorganische und Allgemeine Chemie* **2000**, 626.7, 1519-25. [2] F. Pors, et. al. *Revue Internationale des Hautes Temperatures et des Refractaires* **1988**, 24.4, 239-46. [3] Y. Kim, et. al. *Chemistry of Materials* **2004**, 16.7, 1267-76. [4] S. Ebbinghaus, et. al. *Acta Crystallographica C* **2004**, 60.9, 91-3. [5] M. Stoltzfus, Diss. Ohio State U., **2007**. [6] K. Page, et. al. *Chemistry of Materials* **2007**, 19.16, 4037-42. [7] M. Yang, et. al. *Nature Chemistry* **2010**, 3.1, 47-52.

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Diffuse scattering in substitutionally disordered perovskites

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Perovskites ABO₃ are the subject of an enormous material engineering effort. This reflects the fact that a wide range of physical properties can be gained with different compositions, where both cation sites can be occupied by two or more different species. One of the most prominent examples is that of ferroelectric relaxors, for which mixing cations greatly enhances electromechanical qualities. The variety of properties in these compounds is a derivative of atomic scale phenomena. Therefore, some local probe experiment is an essential part of any structure-property investigation. Diffuse scattering (DS) can be a method of choice for such studies as it contains information about atomic correlations and thus essentially any type of collective phenomena.

The morphology of DS effects in perovskites can be, in most of the cases, related to the symmetry of the most prominent phonon modes.