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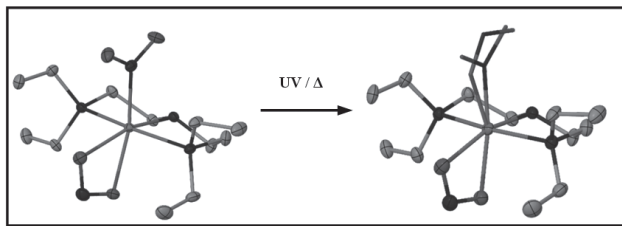
Acta Cryst. (2011) A67, C700**Thermal and photocrystallographic studies on a nickel-nitro complex**

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The technique of time-resolved crystallography has attracted much interest in recent years, as a result of rapid technological advancements in the field. These methods introduce the “fourth dimension” of time into the crystallographic experiment, allowing the structures of short-lived and metastable species to be determined [1].

In this work, nitro-(η^1 -NO₂) to nitrito-(η^1 -ONO) linkage isomerisation in the complex [Ni(Et₄dien)(NO₂)₂] (Et₄dien = N,N,N',N'-tetraethyldiethylenetriamine) has been studied using time-resolved crystallographic techniques. Significant levels of conversion are induced in the single-crystal when the complex is excited both photochemically and thermally. 86% conversion to the metastable nitrito-(η^1 -ONO) linkage isomer is achieved following irradiation with UV light, and a maximum 42% conversion is thermally induced when variable temperature studies are conducted between 100 K and 370 K.

This is the first crystallographic study to report both thermal and photochemical excitation of the nitrite ligand in the same system.



[1] P. Coppens, I.I. Vorontsov, T. Graber, *Acta Cryst. A* **2005**, 61, 162.

Keywords: photocrystallography, photoactivation, nitrite

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Acta Cryst. (2011) A67, C700**Crystal structure and luminescence properties of lanthanide-containing organic complexes**

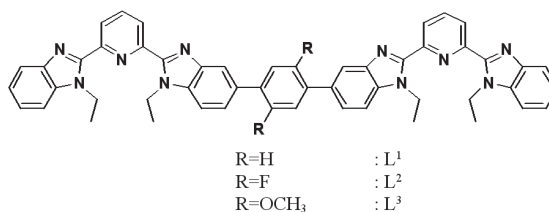
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In order to rationalize and design luminescent lanthanide-containing organic complexes, the central phenyl ring separating 2,6-bis(benzimidazol-2-yl)pyridine binding units in the bis-tridentate model ligands L¹-L³ were substituted with neutral (R=H, L¹), electro-attracting (R=F, L²) or electro-donating (R=OCH₃, L³) groups. Reaction of these ligands with Ln(hfac)₃ salts give poorly soluble dinuclear single strand complexes [Ln₂Lⁱ(hfac)₃] (i=1-3).

X-Ray single crystal structure analyses revealed that the stepwise connection of bulkier substituent onto the central phenyl ring (R=H < R=F ~ R=OCH₃) increases the inter-annular phenyl-benzimidazole interplanar angles (25° < α < 54°). This structural feature is expected to affect the HOMO-LUMO gap in the various complexes (as exemplified by TD-DFT calculations for the ligands in gas-phase).

Solid state photophysical properties on [Eu₂Lⁱ(hfac)₃] (i=1-3)

revealed that the ligand-to-metal energy transfer is significantly affected by the choice of the substituent and we conclude that the electro-attracting substituent F is the best candidate simultaneously matching structural and solution properties, and photophysical characteristics.



Keywords: lanthanide, luminescence, polyaromatic ligands

MS81.P01

Acta Cryst. (2011) A67, C700-C701**Flux growth of piezoelectric single-crystals from the SiO₂-GeO₂ binary diagram**

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Nowadays, synthetic α -quartz is still the most extensively used piezoelectric material. Its zero temperature coefficients cut (AT-cut) and its low acoustic loss are exploited in Surface Acoustic Waves devices (filters, oscillators, resonators...). However, its piezoelectric properties are limited in temperature due to its transition towards the non piezoelectric β -quartz phase, which occurs at 573°C. Besides, its electromechanical coupling coefficient is low (k=11%) considering those obtained by PZT ceramics (k=60-90%).

In order to increase the electromechanical coupling coefficient and the thermal stability domain, the solid-solution between SiO₂ and GeO₂, a quartz analog, was investigated. The main interest of GeO₂ is its high structural distortion: in theory, as regards to previous studies on the α -quartz homeotype family, its piezoelectric performances, linked to distortion, should be three times higher. Furthermore, no α/β -quartz phase transition appears in α -GeO₂. Both parts of the Ge_{1-x}Si_xO₂ solid-solution were studied. The rich SiO₂-content compositions where some Si⁴⁺-substitution by Ge⁴⁺ delay the α/β -quartz phase transition and the rich GeO₂-content compositions where some Ge⁴⁺-substitution by Si⁴⁺ atoms stabilize the α -quartz phase of GeO₂ (metastable at ambient temperature). The increase of the structural distortion in germanium-substituted SiO₂ compositions should also improve their piezoelectric performances.

Single-crystals from both side of the binary SiO₂-GeO₂ diagram have already been synthesized by the hydrothermal method. However, the use of water as growth medium favors the formation of water inclusions in crystals. These inclusions were avoided by the use of a novel way to grow single-crystal of this system: the high-temperature flux growth technique. The growth process was optimized to enlarge the transparent, colorless and well-faceted crystals obtained. Millimeter-size flux-grown Ge_{1-x}Si_xO₂ single-crystals, crystallizing in the trigonal space group P3₁21 or P3₂21, were grown by spontaneous nucleation with the slow cooling method. Different macroscopic morphologies, going from pseudo-cubic shape to hexagonal prism-like shape, were observed depending on the nature of the flux, the substitution content and the sursaturation rate.

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

MS81.P02

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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.

Keywords: hafnium(IV), bidentate ligands, formation kinetics

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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.

Keywords: oxynitride, order/disorder, perovskite

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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.